PB88-198619

Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)-Air Emission Models, Documentation

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Dec 87

U.S Department of Commerce
National Technical information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO EPA/SW/DK-88/046a
EPA-450/3-87-026

2.

3. RE PB88-198619

4. TITLE AND SUBTITLE
Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models

5. REPORT DATE
December 1987

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Air Quality Planning and Standards
Office of Air and Radiation
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-4326

12. SPONSORING AGENCY NAME AND ADDRESS
DAA for Air Quality Planning and Standards
Office of Air and Radiation
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/200/004

15. SUPPLEMENTARY NOTES
For Diskettes, see: PB88-198601

16. ABSTRACT

Analytical models are presented for estimating air emissions form hazardous waste treatment, storage, and disposal facilities (TSDF). Air emission models have been developed for aerated and nonaerated surface impoundments, land treatment facilities, landfills, and wastepiles. Emission model predictions are compared to available field data. This report also includes emission factors for transfer, storage, and handling operations at TSDF.

The models have been assembled into a spreadsheet that is included in this report as floppy diskette for use on a microcomputer.

Appendices include a list of physical-chemical properties for approximately 700 compounds and a comprehensive source list of pertinent literature in addition to that cited in the report.

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
SPRINGFIELD, VA. 22161

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Hazardous Waste Air Emissions TSDF Air Emissions Air Emission Models	Air Pollution	

18. DISTRIBUTION STATEMENT Release unlimited, available from NTIS, 5285 Port Royal Road, Springfield, VA 22161	**19. SECURITY CLASS** *(This Report)* Unclassified	**21. NO. OF PAGES** 350
	20. SECURITY CLASS *(This page)* Unclassified	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-87-026
December 1987

Air

SEPA

Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) — Air Emission Models

EPA-450/3-87-026

Hazardous Waste Treatment, Storage and Disposal Facilities (TSDF) — Air Emission Models

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park NC 27711

December 1987

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CONTENTS

Section | | Page

1.0 Introduction 1-1
1.1 Background 1-1
1.2 Scope 1-2
1.3 Report Organization 1-2

2.0 Description of Pathways 2-1
2.1 General 2-1
2.2 Volatilization 2-2
2.3 Adsorption 2-5
2.4 Migration 2-6
2.5 Runoff 2-7
2.6 Biological Decomposition 2-7
2.7 Photochemical Decomposition 2-8
2.8 Hydrolysis 2-10
2.9 Oxidation/Reduction 2-11
2.10 Hydroxyl Radical Reactions 2-12
2.11 References 2-12

3.0 Importance of Pathways 3-1
3.1 Introduction 3-1
3.2 Theoretical Basis 3-1
3.2.1 Surface Impoundments 3-3
3.2.2 Aerated and Nonaerated Wastewater Treatment 3-3
3.2.3 Land Treatment 3-3
3.2.4 Landfills 3-6
3.3 Emission Models 3-6
3.4 References 3-6

4.0 Surface Impoundments and Open Tanks 4-1
4.1 Narrative Description of Emissions and Model Units 4-1
4.2 Quiescent Surfaces with Flow 4-3
4.2.1 Emission Model Equations 4-3
4.2.2 Model Plant Parameters for Quiescent Impoundments 4-11
4.2.3 Example Calculation for Storage Impoundments 4-12

CONTENTS (continued)

Section Page

4.3 Biodegradation 4-16
4.3.1 Description of Biological Active Systems 4-16
4.3.2 Rate of Biodegradation 4-20
4.3.3 Example Calculation for Quiescent Impoundments 4-27
4.4 Mechanically Aerated Impoundments and Activated Sludge Units 4-29
4.4.1 Emission Model Equations 4-29
4.4.2 Model Plant Parameters for Mechanically Aerated Impoundments 4-30
4.4.3 Example Calculation for Mechanically Aerated Treatment Impoundments........... 4-34
4.4.4 Example Calculation for Activated Sludge Unit 4-40
4.5 Disposal Impoundments with Quiescent Surfaces .. 4-41
4.5.1 Emission Model Equations 4-41
4.5.2 Model Plant Parameters for Disposal Impoundments 4-45
4.5.3 Example Calculations for Disposal Impoundments 4-45
4.6 Diffused Air Systems 4-49
4.6.1 Emission Model Equations 4-49
4.6.2 Model Unit Parameters for Activated Sludge Unit with Diffused Air 4-51
4.6.3 Example Calculation for Diffused Air Activated Sludge Unit 4-51
4.7 Oil Film Surfaces.............................. 4-53
4.8 Discussion of Assumptions and Sensitivity Analysis....................................... 4-55
4.8.1 Removal Mechanisms....................... 4-55
4.8.2 Major Assumptions........................ 4-57
4.8.3 Sensitivity Analysis..................... 4-58
4.9 References...................................... 4-64

5.0 Land Treatment 5-1
5.1 Narrative Description of Land Treatment and Air Emissions 5-1
5.2 Land Treatment 5-3
5.2.1 Land Treatment Emission Model Descriptions 5-3
5.2.1.1 Analytical Correlations.......... 5-3
5.2.1.2 Biodegradation 5-7
5.2.1.3 Estimation of Equilibrium Coefficient, Keq................ 5-8

CONTENTS (continued)

Section Page

5.2.1.4 Estimation of Effective Diffusivity.................... 5-9
5.2.1.5 Waste Partitioning............. 5-10
5.2.1.6 Emissions at Short Times........ 5-11
5.2.1.7 Estimating the Fraction Emitted at Short Times.......... 5-17
5.2.1.8 Estimating the Fraction Emitted for Longer Times........ 5-18
5.2.1.9 Tilling........................ 5-24
5.2.1.10 Model Selection................ 5-25
5.2.2 Waste Application Model 5-26
5.2.3 Oil Film Model 5-26
5.2.4 Model Inputs 5-29
5.2.5 Estimation of Total VO Emissions......... 5-35
5.2.6 Example Calculations 5-36
5.2.6.1 Emissions from Land Treatment Soil 5-36
5.2.6.2 Emissions from Waste Application 5-39
5.2.6.3 Emissions from an Oil Layer on Soil Prior to Tilling 5-42
5.2.7 Assumptions and Sensitivity Analyses 5-43
5.3 References 5-45

6.0 Landfills and Wastepiles 6-1
6.1 Introduction 6-1
6.2 Closed Landfills 6-1
6.2.1 Emission Model Equations 6-1
6.2.2 Model Plant Parameters for Closed Landfills 6-14
6.2.3 Example Calculation for Closed Landfill.................................. 6-17
6.3 Fixation Pits 6-21
6.3.1 Emission Model Equations 6-21
6.3.2 Model Plant Parameters for Fixation Pits 6-30
6.3.3 Example Calculation for Fixation Pit 6-31
6.4 Open Landfills and Wastepiles 6-33
6.4.1 Emission Model Equations 6-33
6.4.2 Model Plant Parameters for Open Landfills and Wastepiles 6-40
6.4.2.1 Parameters for Open Landfills... 6-40
6.4.2.2 Parameters for Wastepiles....... 6-41
6.4.3 Example Calculation for Open Landfill 6-43
6.5 References 6-47

CONTENTS (continued)

Section Page

7.0 Transfer, Storage, and Handling Operations 7-1
7.1 Narrative Description of Model Plants and Emissions 7-1
7.2 Container Loading 7-1
7.2.1 Emission Model for Container Loading 7-1
7.2.2 Model Parameters 7-2
7.2.3 Sample Calculation for Tank Loading 7-2
7.3 Container Storage 7-5
7.3.1 Emission Model for 55-Gal Drums, Tank Trucks, and Railroad Tank Cars 7-5
7.3.2 Model Parameters for Drum Storage 7-6
7.3.3 Sample Calculations for Drum Storage 7-6
7.3.4 Emission Model for Open Dumpsters 7-7
7.3.5 Model Parameters for Open Dumpster Storage 7-7
7.3.6 Sample Calculation for Open Dumpster Storage 7-8
7.4 Container Cleaning 7-9
7.4.1 Emission Model for Container Cleaning 7-9
7.4.2 Model Parameters 7-10
7.4.3 Sample Calculation for Tank Truck Cleaning 7-11
7.5 Stationary Tank Loading 7-11
7.5.1 Emission Model for Stationary Tank Model 7-11
7.5.2 Model Parameters 7-12
7.5.3 Sample Calculation for Tank Loading Emission Model 7-13
7.6 Stationary Tank Storage 7-15
7.6.1 Model Description 7-15
7.6.2 Model Parameters 7-15
7.6.3 Sample Calculation for Tank Storage Emission Model 7-17
7.7 Spills 7-18
7.7.1 Model Description 7-18
7.7.2 Model Parameters 7-18
7.7.3 Sample Calculation for Drum Storage Model 7-18
7.8 Fugitive Emissions 7-19
7.8.1 Emission Model for Fugitives 7-19
7.8.2 Model Parameters 7-20
7.8.3 Sample Calculation for Fugitive Emission Model 7-20
7.9 Vacuum Truck Loading 7-20
7.9.1 Emission Model for Vacuum Truck Loading 7-20

CONTENTS (continued)

Section Page

7.9.2 Model Parameters 7-21
7.9.3 Sample Calculation 7-21
7.10 References 7-23

8.0 Comparison of Model Results with Field Test Data 8-1
8.1 Introduction 8-1
8.2 Surface Impoundments and Open Tanks 8-1
8.2.1 Summary 8-1
8.2.2 Details of Comparisons 8-2
8.2.3 Recommendations for Additional Data 8-17
8.3 Land Treatment 8-19
8.3.1 Midwest Refinery--1985 (Case 1).......... 8-29
8.3.2 West Coast Refinery (Case 2)............. 8-34
8.3.3 Commercial Waste Disposal Test (Case 3).. 8-34
8.3.4 Midwest Refinery--1979 (Case 4).......... 8-34
8.4 Landfills and Wastepiles......................... 8-34
8.5 Transfer, Storage, and Handling Operations 8-39
8.5.1 Models Documented in AP-42 8-39
8.5.2 Fugitive Emissions 8-44
8.5.3 Spillage 8-44
8.5.4 Open Dumpster Storage Emissions 8-44
8.6 References 8-44

Appendix A CHEMDAT6 User's Guide.............................. A-1

Appendix B A Guide Through the Literature...................... B-1

Appendix C Comprehensive Source List........................... C-1

Appendix D Properties for Compounds of Interest................ D-1

FIGURES

Number Page

6-1 Fick's law correction factor F_y as a function of y*.. 6-24

8-1 Estimated vs. measured benzene emission flux rates--Case 1.. 8-25
8-2 Estimated vs. measured toluene emission flux rates--Case 1.. 8-26
8-3 Estimated vs. measured toluene emission flux rates--Case 2 (data for 4 days only)................ 8-27
8-4 Estimated vs. measured total VO emission flux rates--Case 2.. 8-28
8-5 Estimated vs. measured VO emission flux rates--Case 3.. 8-30
8-6 Estimated vs. measured emission flux rates--Case 4.. 8-31

TABLES

Number Page

2-1 Values of Constants for Use in Equation (2-4)........ 2-4

3-1 Pathways for Hazardous Waste Area Emission Sources... 3-2
3-2 Statistics for Surface Water Pathways............... 3-4
3-3 Pathways for TSDF Sites............................ 3-5

4-1 Equations for Calculating Individual Mass Transfer Coefficients for Volatilization of Organic Solutes from Quiescent Surface Impoundments................. 4-6
4-2 Input Parameters--Storage Impoundment............... 4-13
4-3 Design Parameters for Activated Sludge Processes..... 4-17
4-4 Impoundments Designed for Biodegradation............ 4-19
4-5 Typical or Default Values for Biomass Concentration... 4-21
4-6 Equations for Calculating Individual Mass Transfer Coefficients for Volatilization of Organic Solutes from Turbulent Surface Impoundments.. 4-31
4-7 Input Parameters--Treatment Impoundments (Mechanically Aerated)............................. 4-35
4-8 Input Parameters--Mechanically Aerated Activated Sludge Unit... 4-42
4-9 Intermediate and Final Calculation Results for Activated Sludge Model Unit......................... 4-43
4-10 Input Parameters--Disposal Impoundments............. 4-46
4-11 Input Parameters--Diffused Air Activated Sludge Unit... 4-52
4-12 Results of Sensitivity Analysis for Quiescent Storage Impoundment................................. 4-61
4-13 Results of Sensitivity Analysis for Mechanically Aerated Impoundments................................ 4-62
4-14 Results of Sensitivity Analysis for Disposal Impoundments.. 4-63

5-1 Comparison of the Estimated Fraction Emitted Using Three Different Equations (Integrated Flux from Soil).. 5-5
5-2 Emission Estimates Using Two Different Equations for the Vapor-Soil Partition Coefficient... 5-12
5-3 RTI Model for Land Treatment Emissions.............. 5-13

TABLES (continued)

Number		Page
5-4	Estimated Air Emission Fraction at Long Times........	5-21
5-5	Rigorous vs. Approximate Estimates of Emission Fractions..	5-22
5-6	Waste Application Emission Model.....................	5-27
5-7	Oil Film Surface Emission Model......................	5-30
5-8	Measured and Estimated Biorates and Decay Constants for Selected Organic Constituents..........	5-34
5-9	Estimated Emission Rates and Fractions Emitted Versus Time for Example Land Treatment Calculation..............................	5-40
6-1	RTI Closed Landfill Model............................	6-10
6-2	Input Parameters--Closed Landfill....................	6-16
6-3	Fick's Law Correction Factor as a Function of y*.....	6-23
6-4	Open Dump Model......................................	6-28
6-5	Input Parameters--Fixation Pit.......................	6-32
6-6	RTI Land Treatment Model Applied to Open Landfills and Wastepiles (No Biodegradation).........	6-37
6-7	Input Parameters--Open Landfill......................	6-42
6-8	Input Parameters--Wastepiles.........................	6-44
7-1	S Factors for Calculating Petroleum Loading Losses..	7-3
7-2	Pertinent Fixed-Roof Tank Specifications.............	7-14
7-3	Paint Factors for Fixed-Roof Tanks...................	7-16
7-4	SOCMI Emission Factors for Fugitive Losses...........	7-19
8-1	Comparison of Results for Reducing Lagoon 1 at Site 5..	8-3
8-2	Comparison of Results for Holding Pond 6 at Site 5..	8-4
8-3	Comparison of Results for Oxidizing Lagoon 2 at Site 5..	8-5
8-4	Comparison of Results for Surface Impoundment at Site 4..	8-5
8-5	Comparison of Results for Wastewater Holding Lagoon at Site 3....................................	8-7
8-6	Comparison of Results for Primary Clarifiers at Site 8..	8-7
8-7	Comparison of Results for Equalization Basin at Site 8..	8-8
8-8	Comparison of Results for Aerated Stabilization Basins at Site 8....................................	8-8
8-9	Comparison of Results for Covered Aerated Lagoon at Site 7..	8-10

TABLES (continued)

Number Page

8-10 Description of Petrasek's Activated Sludge System... 8-12
8-11 Comparison of Petrasek's Measurements and Model Predictions.................................. 8-13
8-12 Description of Two Chicago Activated Sludge Units.... 8-15
8-13 Comparison of Measured and Predicted Effluent Concentrations for Chicage Wastewater Treatment Plants... 8-16
8-14 Comparison of Biorates............................... 8-18
8-15 Summary of Land Treatment Testing and Test Results... 8-20
8-16 Input Parameters for RTI Land Treatment Model........ 8-32
8-17 Measured and Estimated Emissions--Case 1............ 8-33
8-18 Input Parameters for RTI Land Treatment Model........ 8-35
8-19 Estimated vs. Measured Emissions--Case 2............ 8-35
8-20 Input Parameters for RTI Land Treatment Model........ 8-36
8-21 Estimated vs. Measured Total VO Emissions--Case 3.. 8-36
8-22 Input Parameters for RTI Land Treatment Model........ 8-37
8-23 Estimated vs. Measured Emissions--Case 4............ 8-37
8-24 Model Input Parameters Used in Application of the RTI Land Treatment Model to an Active Landfill at Site 5................................. 8-40
8-25 Comparison of Measured and Predicted Emission Rates for Site 5 Active Landfill.................... 8-41
8-26 Model Input Parameters Used in Application of the RTI Land Treatment Model to an Active Landfill at Site 8.......................... 8-42
8-27 Comparison of Measured and Predicted Emission Rates for the Site 8 Active Landfill................ 8-43

1.0 INTRODUCTION

1.1 BACKGROUND

This report was prepared for the Environmental Protection Agency's (EPA's) Office of Air Quality Planning and Standards (OAQPS) as part of the effort to develop air emission models for hazardous waste treatment, storage, and disposal facilities (TSDF). Basic to this effort is the determination of the means by which volatile organics (VO) escape to the environment from TSDF.

VO in surface impoundments, land treatment facilities, landfills, wastepiles, or wastewater treatment (WWT) plant effluents can depart through a variety of pathways, including volatilization, biological decomposition, adsorption, photochemical reaction, and hydrolysis. To allow reasonable estimates of VO disappearance, one must know which pathways predominate for a given chemical, type of waste site, and set of meteorological conditions.

Analytical models have been developed to estimate emissions of VO via various pathways from area emission sources at hazardous waste sites. Some of these models have been assembled into a spreadsheet that is included in this report as a floppy diskette for use on an IBM PC, or compatible, microcomputer. A user's guide for these models is included in the report as Appendix A. Area emission sources for which models are included on the diskette are as follows:

- Nonaerated impoundments, which include quiescent surface impoundments and open top WWT tanks
- Aerated impoundments, which include aerated surface impoundments and aerated WWT tanks
- Disposal impoundments, which include nonaerated disposal impoundments
- Land treatment
- Landfills.

These models can be used to estimate the magnitude of site emissions for regulatory purposes. Sample calculations using each model also are included in this report.

1.2 SCOPE

This report briefly describes the chemical and physical pathways for VO and discusses their importance for different types of sites and sets of conditions. Models developed for estimating the relative magnitude of environmental release in the presence of competing pathways are presented, and physical characteristics of the parameters that serve as inputs to the models are identified.

The models provide an estimate of the relative magnitude of VO pathways on a compound-specific basis. Models for aerated and nonaerated impoundments, lagoons, landfills, wastepiles, and land treatment facilities have been installed in an integrated spreadsheet program, CHEMDAT6, which allows a user to calculate the partitioning of VO among various pathways depending on the particular parameters of the facility of interest. The program is structured to allow new data (e.g., compounds and model facility parameters) to be added (see Appendix A for user's guide). The results of the calculated partitioning may be used to identify those characteristics that are important in determining relative VO loss rates.

Source variability will significantly influence the relative importance of the pathways. For highly variable sources, it may be possible to exclude insignificantly small pathways from consideration. The relative magnitude of these pathways then can be compared by applying the methodology to a model facility to determine relative differences among various compounds.

1.3 REPORT ORGANIZATION

Section 2.0 describes each of the potential pathway mechanisms that determine the fate of various chemical species. Section 3.0 discusses the importance of the pathways for surface impoundments and aerated and non-aerated WWT facilities, land treatment sites, and landfills/wastepiles. Sections 4.0, 5.0, and 6.0 describe the emission models applicable to these sites. Models for estimating emissions from transfer, storage, and handling operations are described in Section 7. Section 8 compares emission model predictions with the field data that are available.

This report compares relative rates of VO destruction and volatilization to determine the most significant pathways. The rate of VO volatilization destruction for any one pathway is calculated so that it can be expressed as a fraction of the loss/destruction from all pathways.

Appendix B contains supplementary material, and Appendix C presents a comprehensive source list that includes pertinent literature in addition to that cited in the sections and appendixes of this report.

Properties of compounds of interest to TSDF pathways and emission estimation are presented in Appendix D. A subset of these compounds is a part of CHEMDAT6. The user's guide, Appendix A, describes the procedures that are used in estimating emissions using CHEMDAT6 and other procedures presented in the body of the report. The user's guide also contains instructions for modifying CHEMDAT6 to include additional compounds using the compound characteristics presented in Appendix D.

2.0 DESCRIPTION OF PATHWAYS

2.1 GENERAL

A pathway is considered here to be any process that removes volatile organics from a site. The removal may be physical (as in volatilization of a solvent from a surface impoundment) or chemical (as in oxidation of an alcohol in a wastewater treatment plant).

Pathways may be considered as rate processes, with rate often strongly dependent on concentration of the disappearing species and temperature of the system. Rates vary in order from zero to mixed, with perhaps first order predominating, that is:

$$\text{rate} = -\frac{dc}{dt} = k_v c \qquad (2\text{-}1)$$

where

c = concentration of disappearing substance, g/L

t = time, s

k_v = volatilization constant, s^{-1}

Half-life, the time required for one-half of the substance to disappear, is a useful concept. It provides an easily visualized measure of the time required for disappearance. For a first-order rate process:

$$t_{1/2} = (\ln 2) k_v^{-1} = 0.693\ k_v^{-1} \qquad (2\text{-}2)$$

where

$t_{1/2}$ = half-life, s.

The half-life of a second-order equation is as follows:

$$t_{1/2} = k_v'^{-1}\ C_o^{-1} \qquad (2\text{-}3)$$

where

k_v' = second-order volatilization constant, L/(g•s)

C_o = initial concentration, g/L.

Note that first-order half-lives are independent of initial concentration while higher order half-lives are not.

Much of the following material is taken from ICF.[1] The pathways described are physical (volatilization, adsorption, migration, and runoff) and chemical (biological decomposition, photochemical decomposition, hydrolysis, oxidation/reduction, and hydroxyl radical reaction).

2.2 VOLATILIZATION

Volatilization occurs when molecules of a dissolved substance escape to an adjacent gas phase. The driving force for this process in nonturbulent liquids is molecular diffusion. Equation (2-1) shows the rate of volatilization of an organic chemical from water. For this case, the rate constant can be estimated:[2]

$$k_v = \frac{1}{L}\left[\frac{1}{k_l^o(D_l^c/D_l^o)^m} + \frac{R\ T}{(10^6)Hk_g^w(D_g^c/D_g^w)^n}\right]^{-1} \qquad (2\text{-}4)$$

where

L = mixing depth of water, cm

k_l^o = mass transfer coefficient of oxygen in water, cm/s

D_l = diffusion coefficient of the chemical (c) or oxygen (o) in water, cm^2/s

m = liquid turbulence exponent, 0.5 to 1, dimensionless, from Table 2-1

R = ideal gas constant, atm $cm^3/(mol•K)$

T = temperature, K

H = Henry's law constant, atm m^3/mol

k_g^w = mass transfer coefficient for water vapor in air, cm/s

D_g = diffusion coefficient of the chemical (c) or water (w) in air, cm^2/s

$\bar{n}$ = gas turbulence exponent, 0.5 to 1.0, dimensionless, from Table 2-1.

Equation (2-4) requires values of diffusion coefficients and Henry's law constants. If tabulated values are not available, the following estimations can be used. For the diffusion of a chemical in air:[3]

$$D_g = 0.0067T^{1.5} \left(0.034 + M^{-1}\right)^{0.5} M^{-0.17} \left[(M/2.5d)^{0.33} + 1.81\right]^{-2} \qquad (2\text{-}5)$$

where

M = molecular weight of chemical, g/g mol

d = density of liquid chemical, g/cm^3.

For diffusion coefficients in water:

$$D_l = 1.518 \, (10^{-4}) \, V_{cm}^{-0.6} \qquad (2\text{-}6)$$

where

V_{cm} = molar volume of chemical, cm^3/g mol.

This equation assumes the system temperature to be 300 K. For other temperatures, a more rigorous form of the equation should be used, as in Perry.[4] Molar volume is estimated as the ratio of molecular weight to liquid density at room temperature.

If ideal gases and solutions are assumed, Henry's law constant can be estimated from:

$$H = P/(14.7s) \qquad (2\text{-}7)$$

where

P = pure component vapor pressure, psia

s = solubility of chemical in water, g mol/m^3.

Values for other terms in Equation (2-4) have been tabulated by ICF and are given in Table 2-1.

In general, equations are available to estimate volatilization from wastewater treatment systems and surface impoundments.[6,7] In the case of land treatment and landfills, the models for volatilization are much less well developed and the supporting data are more limited than those of the

TABLE 2-1. VALUES OF CONSTANTS FOR USE IN EQUATION (2-4)[5]

Constant	Value Rivers	 Lakes
L (cm)	200	200
k_l^o (cm•s^{-1})	0.0022	0.0005
m	0.7	1.0
T (K)	293	293
RT (m^3•atm•mol^{-1})	2.40×10^{-2}	2.40×10^{-2}
K_g^W (cm•s^{-1})	0.58	0.58
n	0.7	0.7

aqueous systems. The rate of volatilization at a soil-air interface is a function of the concentration and properties of the escaping chemical, soil properties (moisture, temperature, clay, and organic content), and properties of the air at soil level (temperature, relative humidity, and wind speed).[8]

2.3 ADSORPTION

Adsorption takes place when molecules of a dissolved chemical (in a liquid-solid system) become physically attached to elements of the solid phase. Chemical bonding may also occur (chemisorption). An example of adsorption is molecules of solvent being sorbed by particles of silt in a surface impoundment. If the adsorptive capacity of the solid material is reached, no further net sorption will occur. With reductions in concentration in the bulk liquid of the chemical being sorbed (adsorbate), desorption may take place. The amount of material adsorbed depends on (1) the concentration of adsorbate, (2) the amount of solid phase (adsorbent), and (3) the temperature. For systems with constant adsorbent properties, primarily surface area per unit mass, the amount of material adsorbed at a particular concentration and temperature is proportional to the mass of adsorbent. For example, the Freundlich adsorption isotherm equation allows prediction of amount adsorbed as follows:

$$\frac{X}{m} = K_f C'^{1/n} \qquad (2\text{-}8)$$

where

X = mass of chemical adsorbed, g

m = mass of adsorbent, g

K_f = Freundlich adsorption coefficient, (g sorbate/g sorbent)/(g sorbate/g solution)

C' = concentration of chemical in solution at equilibrium, g sorbate/g solution

n = empirical constant, ranging from 0.7 to 1.1, typically 1.0 for soils, dimensionless.

A Langmuir adsorption isotherm can be derived from a kinetic rate theory describing the adsorption and desorption rates. The rate of adsorption is proportional to the rate of collisions between adsorbate molecules and free adsorbent surface. The rate decreases with lowering adsorbate concentration and with decreasing surface sites available for adsorbing molecules. The following rate equation applies:

$$\text{Rate of adsorption} = k_1 C' (1-f) \qquad (2\text{-}9)$$

where

k_1 = rate constant for adsorption, g/s

f = fraction of adsorption sites occupied, dimensionless.

For desorption:

$$\text{Rate of desorption} = k_2 f \qquad (2\text{-}10)$$

where

k_2 = rate constant for desorption, g/s.

At equilibrium the two rates are equal, and

$$f = \frac{k_1 C'}{k_1 C' + k_2} \quad . \qquad (2\text{-}11)$$

Adsorption rates are usually rapid compared to the other processes discussed here. However, mass transfer limitations may reduce effective rates, especially for poorly mixed systems. Lack of sorbent and its saturation may also reduce the effectiveness of adsorption.

For estimating adsorption partitioning, a linear relationship is assumed ($n = 1$ or $k_1 C \ll k_2$). The equilibrium relationship for biomass is estimated from an equation of Matter-Muller,[9] based on the logarithm of the octanol-water partition coefficient, LOW. For land treatment and landfills, the only partitioning of importance to fate predictions is gas-liquid partitioning.

2.4 MIGRATION

Migration occurs when chemicals applied to soils are transported through the soils to groundwater. Leaching and percolation are the mechanisms that physically remove chemical molecules from a point of deposit and carry them toward a water table. Capillary flow is a resisting mechanism that moves the molecules upward through the soil. The leachability of a chemical is a function of soil texture and cation exchange capacity, amount of soil organic content, amount and intensity of rainfall, and mechanical placement and adsorptive properties of the chemical.[10]

2.5 RUNOFF

Chemicals at or near the soil may be washed away by rain. The rate depends on soil and chemical characteristics and on rainfall rates and frequency. Clark, Viessman, and Hammer[11] state that runoff in any drainage area is a function of climate and the physical characteristics of the area. Significant factors include precipitation type; rainfall intensity, duration, and distribution; storm direction; antecedent precipitation; initial soil moisture conditions; soil type; evaporation; transpiration; and, for a given drainage area, its size, shape, slope, elevation, directional orientation, and land use characteristics. If rainfall is heavy shortly after application of a chemical, runoff and erosion can physically remove it. The chemical may be dissolved in runoff water, carried along by it, or adsorbed on eroding soil particles that move with runoff. For pesticide applications, about 3 to 10 percent of the applied material appears in runoff water. Below a certain intensity, rainfall will promote leaching of nonadsorbed chemical into the ground rather than result in runoff.

2.6 BIOLOGICAL DECOMPOSITION

Biological decomposition takes place when microbes break down organic compounds for metabolic processes. The rate of decomposition depends on the structure of the compound and on the needs of the microbes. If the compound is present in excess, the rate of population increase is as follows:

$$dx/dt = Rx \tag{2-12}$$

where

x = concentration of biomass, g/L

R = specific growth rate coefficient, s^{-1}.

If the compound is present in limited amount, the rate becomes a hyperbolic saturation function of the compound (substrate) concentration:[12]

$$\frac{dx/dt}{x} = R_{max}\, S/(K_s + S) \tag{2-13}$$

where

R_{max} = maximum specific growth rate coefficient (where substrate is in excess), s^{-1}

S = concentration of substrate, g/L

K_s = substrate concentration at which the rate of substrate utilization is one-half of the maximum rate, g/L.

Because the microbial population increases at the expense of the compound, the growth rate is proportional to the compound's rate of disappearance. The rate process may be of zero, first, or mixed order depending on concentration of the substrate. In the presence of multiple substrates, kinetics become complex.

For the case of S much greater than K_s, the equation approaches zero order, and Equation (2-13) becomes:

$$\frac{dx/dt}{x} = R_{max} \quad . \tag{2-14}$$

For S much less than K_s, the equation approaches first order:

$$\frac{dx/dt}{x} = SR_{max}/K_s \tag{2-15}$$

with R_{max}/K_s being the first-order rate constant.

For intermediate values of S, the equation is mixed order, with the order dependent on values of the constants R_{max} and K_s.

2.7 PHOTOCHEMICAL DECOMPOSITION

Photochemical decomposition may occur in two ways. A chemical may absorb light and react (direct photolysis), or the chemical may react because of light absorption by surrounding elements (indirect photolysis).

For direct photolysis, the rate of reaction of a dilute solution of chemical in pure water is as follows:

$$K_p = b\,\Phi\,\Sigma\,\epsilon_\lambda I_\lambda [C], \qquad (2\text{-}16)$$

where

K_p = rate of direct photolysis, g/(L s)

b = unit conversion constant, 3.8×10^{-21} g mol cm^4/(L photon)

Φ = reaction quantum yield, dimensionless

ϵ_λ = light absorption coefficient at wavelength interval λ, L/(g mol•cm)

I_λ = light flux at wavelength interval λ, photons/(cm^3•s)

C = concentration of the chemical in water, g/L.

Lyman[13] refers to Zepp and Cline;[14] Zepp;[15] and Mabey, Mill, and Hendry[16] for details of rate calculations in aquatic systems. In these systems, the rate constant K_p varies with the distribution of sunlight and its intensity. Time of day, season, cloud cover, and latitude all affect K_p so that a reference condition must be stated; e.g., a light flux of photons per second corresponding to a cloudless yearly average at a latitude of 40°N.

Reactions may be photocatalyzed. For example, a TiO_2 catalyst can be photoexcited by light at wavelengths less than 360 mm. Ollis[17] examined the degradation of halogenated hydrocarbons with this catalyst and found a rate equation of the form:

$$\frac{1}{dC/dt} = \frac{1}{k_p} + \frac{1}{k_p K_b C} \qquad (2\text{-}17)$$

where

k_p = photolysis rate constant, g chemical/(L•s•g catalyst)

K_b = apparent binding constant of a reaction intermediate adsorbed on the illuminated catalyst surface, L/g chemical.

For 11 halocarbons, values of k ranged from 5.8×10^{-8} to 2.3×10^{-6} g/L•s•g of catalyst, with most about 2.8×10^{-7} to 1.7×10^{-6}. A twelfth halocarbon had a k value of 2.3×10^{-4}. Values of K_b for the 12 compounds ranged from 2 to 20 L/g.

2.8 HYDROLYSIS

Hydrolysis occurs when a chemical reacts with water. For organic compounds, the reaction usually replaces a functional group (X) with a hydroxyl:[18]

$$RX + H_2O = ROH + HX \ . \tag{2-18}$$

Reaction rate constants may be pH-dependent; for a specific pH:

$$k_H = k_a [H^+] + k_n + k_b [OH^-] \tag{2-19}$$

where

k_H = first-order hydrolysis rate constant, s^{-1}

k_a = second-order rate constant for acid-promoted hydrolysis, $L/(g\ mol \bullet s)$

$[H^+]$ = hydrogen ion concentration, g mol/L

k_n = first-order rate constant for pH-independent neutral hydrolysis, s^{-1}

k_b = second-order rate constant for base-promoted hydrolysis, $L/(g\ mol \bullet s)$

$[OH^-]$ = hydroxyl ion concentration, g mol/L.

If

$$k_w = [H^+] [OH^-] \tag{2-20}$$

where

k_w = ionization constant for water $\approx 10^{-14}$ g mol^2/L^2.

Equation (2-19) can be transformed to:

$$k_H = k_a [H^+] + k_n + k_b k_w/[H^+] \ . \tag{2-21}$$

The rate constant k_H depends on system pH and on the relative values of k_A, k_b, and k_n.

2.9 OXIDATION/REDUCTION

Organic compounds in aquatic systems may be oxidized by oxygen (particularly as singlet oxygen, $^1O_2$) or other oxidants such as hydroxyl radicals (OH) and peroxy radicals (RO_2). The OH radicals tend to be very reactive, but present only in low concentrations. The RO_2 radicals are less reactive than the OH radicals, but are present in greater concentrations. Singlet oxygen is highly reactive, but also selective. It has an affinity for electron-rich structures such as dienes and substituted olefins.

The oxidation rate can be calculated as:[19]

$$\frac{dC}{dt} = C\,(k_{RO_2}\,[RO_2] + k_{SO}\,[^1O_2] + k_x\,[X]) \qquad (2\text{-}22)$$

where

k_{RO_2} = rate constant for peroxy radicals, L/(g mol•s)

$[RO_2]$ = concentration of peroxy radicals, g mol/L

k_{SO} = rate constant for singlet oxygen, L/(g mol•s)

$[^1O_2]$ = concentration of singlet oxygen, g mol/L

k_x = rate constant for "other" oxidants, L/(g mol•s)

$[X]$ = concentrations of "other" oxidants, g mol/L.

In anaerobic environments, reduction reactions may take place. Organochlorines are particularly affected. The reduction rate can be calculated as:[20]

$$\frac{dC}{dt} = C \sum_i k_i\,[R_i] \qquad (2\text{-}23)$$

where

k_i = rate constant for reductant i, L/g mol•s

$[R_i]$ = concentration of reductant i, g mol/L.

2.10 HYDROXYL RADICAL REACTIONS

Hydroxyl radical reactions may occur through addition of a hydroxyl radical, abstraction of a hydrogen atom, or both. In the addition, reaction molecules with high electron density portions attract electrophilic hydroxyl radicals. Hydrogen abstraction takes place when a carbon-hydrogen bond in an organic molecule is easily broken; it is controlled by electronic configuration and number of hydrogen reactions in the molecule. The rate constant for the reaction is often in the range of 6 to 60 x 10^8 L/(g mol•s).

A hydroxyl radical reaction rate can be calculated as:[21]

$$\frac{dC}{dt} = k_{OH} [OH^-] C \qquad (2\text{-}24)$$

where

k_{OH} = rate constant for hydrogen abstraction or hydroxyl addition, L/(g mol•s).

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3.0 IMPORTANCE OF PATHWAYS

3.1 INTRODUCTION

The importance of the nine pathways described in Section 2.0 for surface impoundment, open tanks, land treatment facilities, landfills, and wastepiles is described in this section. The discussion centers on the pathways used in the emission models described in subsequent sections. The pathways described in Section 2.0 are repeated below for convenience:

- Volatilization
- Adsorption
- Migration
- Runoff
- Biological decomposition
- Photochemical decomposition
- Hydrolysis
- Oxidation/reduction
- Hydroxyl radical reaction.

Section 3.2 presents the relative importance of these pathways based on the theoretical discussions appearing in Section 2.0, the data appearing in the literature, and engineering judgment. Section 3.3 summarizes in tabular form the results of the emission model analyses in Sections 4.0 through 6.0 and the pathways forming the basis for the emission models.

3.2 THEORETICAL BASIS

The relative importance of the nine pathways for TSDF is discussed in the following text and summarized in Table 3-1. These data were used as

TABLE 3-1. PATHWAYS FOR HAZARDOUS WASTE AREA EMISSION SOURCES[a]

Pathway	Surface impoundments	Wastewater treatment plants		Land treatment	Landfill
		Aerated	Nonaerated		
Volatilization	I	I	I	I	I
Biodegradation	I	I	I	I	S
Photodecomposition	S	N	N	N	N
Hydrolysis	S	S	S	N	N
Oxidation/ reduction	N	N	N	N	N
Adsorption	N	S	S	N	N
Hydroxyl radical reaction	N	N	N	N	N
Migration[b]	N	N	N	N	N
Runoff[b]	N	N	N	N	N

I = Important.
S = Secondary.
N = Negligible or not applicable.

[a] Individual chemicals in a given site type may have dominant pathways different from the ones shown here.

[b] Water migration and runoff are considered to have negligible effects on ground and surface water in a properly sited, operated, and maintained RCRA-permitted hazardous waste treatment, storage, and disposal facility.

the basis for the emission models contained in CHEMDAT6. Results of exercising these models to identify pathways of importance are discussed in Sections 4.0 through 7.0 and are summarized in Section 3.3. A short discussion of the theoretical basis for pathways selection follows. Appendix B presents a more detailed discussion.

3.2.1 Surface Impoundments

Data reported by ICF show predominant removal mechanisms and half-lives for 71 chemicals. Table 3-2 lists the mechanisms and statistics for six surface water pathways. Average half-lives range from about 1/2 to 8 days, with predominant mechanisms being volatilization and biodegradation. The rate of photodecomposition depends on the depth of the surface impoundment. The rate is negligibly low for depths as great as 3 meters and is indicated in Table 3-1 as S for a secondary effect.

3.2.2 Aerated and Nonaerated Wastewater Treatment

As in the case of the surface impoundments, volatilization and biodegradation are potentially significant mechanisms. The relative rates of these mechanisms depend on the particular component and treatment system. Photodecomposition is not expected to be a significant pathway due to the opacity of the system, the depth of the liquid, and the residence time of the processes. Adsorption is not expected to be significant except for large loadings of suspended solids and oils in the wastewater. The concentrations for many VO are expected to be roughly the same in the biomass as in the aqueous phase.

3.2.3 Land Treatment

Based on available emission data and literature sources, volatilization and biodegradation are expected to be important in land treatment.[2-6] For highly volatile constituents, volatilization is expected to be the predominant pathway; for low volatile constituents, biodegradation is expected to be the predominant pathway. Adsorption of organic compounds onto organic carbon in the soil also occurs at land treatment sites. However, calculations of land treatment air emissions both with and without consideration of adsorption show a difference of only 10 percent. Therefore, adsorption is not considered a major pathway for organics removal.

The method of waste application and incorporation into the soil influence the importance of photochemical reactions in the degradation of

TABLE 3-2. STATISTICS FOR SURFACE WATER PATHWAYS

	Pathway					
	Volatilization	Biodegradation	Photodecomposition[a]	Hydrolysis	Oxidation/ reduction	Adsorption
Range of half-lives, days	0.9-15	0.04-96	0.04-900	0.0003-35	0.1-5	0.04-1.5
Average half-life	2.24	8.05	76.3 1.37	5.39	2.05	0.55
Standard deviation	2.85	19.4	259.0 1.82	10.8	2.40	0.83
Number of chemicals	38	26	12	11	4	3

[a] Statistics are given for chemicals with and without an outlier.

TABLE 3-3. PATHWAYS FOR TSDF SITES

Type of facility	Pathways included in model
Quiescent storage and treatment impoundments	Volatilization
Mechanically aerated impoundments	Volatilization Biodegradation
Quiescent disposal impoundments	Volatilization
Land treatment facilities	Volatilization Biodegradation
Closed landfills	Volatilization (diffusion through cap) Barometric pumping
Active landfills	Volatilization (diffusion through waste)
Wastepiles	Volatilization

organic wastes in land treatment facilities.[7] Photodecomposition can occur in land treatment between application and tilling (usually 24 hours), although exposure to sunlight is limited to daylight hours. While exact rates of photodegradation are not known, they are expected to be low. The oil in which the hazardous materials are suspended is semiopaque to sunlight, which would tend to keep photodecomposition low. After tilling, photodegradation is nonexistent because sunlight does not penetrate the soil surface.[8] Consequently, photodecomposition is not expected to be significant.

3.2.4 Landfills

Volatilization is expected to be a primary VO pathway for landfills. Biodegradation is expected to be negligible for hazardous waste landfills. The toxic properties of the water are expected to inhibit biological processes and therefore biodegradation.[9]

Rates of diffusion in the gas phase may be important. Components can diffuse through unsaturated soils (air pockets present). Control of liquid infiltration into the landfill is expected to keep migration into the soil at a negligible level.

3.3 EMISSION MODELS

Based on the exercise of CHEMDAT6 in predicting and comparing pathways for TSDF processes, the pathways shown in Table 3-3 are used as the basis of the models. Insignificant emissions or inadequate data upon which to develop the model relationships are the principal reasons for limiting the models to the pathways shown in Table 3-3.

It should be noted that CHEMDAT6 includes provisions to activate the unused pathways should further investigations and field tests indicate the desirability of incorporating additional pathways in the emission models.

3.4 REFERENCES

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4.0 SURFACE IMPOUNDMENTS AND OPEN TANKS

This section discusses the approach used to estimate air emissions from surface impoundments and open top tanks. The emission models are described, model facilities are defined, and example calculations are presented.

4.1 NARRATIVE DESCRIPTION OF EMISSIONS AND MODEL UNITS

Emissions from surface impoundments and open tanks originate from the uncovered liquid surface that is exposed to the air. The model used to estimate emissions from the liquid surface is based on an overall mass transfer coefficient that incorporates two resistances to mass transfer in series--the liquid-phase resistance and the gas-phase resistance. Numerous correlations are available to estimate the individual mass transfer coefficients (or resistances), and they depend upon the compound's properties and the system's parameters. The recommended correlations and their applicability are described in subsequent sections. The emission estimating procedure also incorporates a flow model that describes the method of operation. For flowthrough systems, the impoundment's or tank's contents may be completely mixed, plug flow, or somewhere in between with varying degrees of backmixing or axial dispersion. Biologically active impoundments and aeration tanks can be designed for either completely mixed or plug flow, and both types of flow models are discussed for these types of systems. For disposal impoundments, the contents are assumed to be well mixed, and the bulk concentration is expressed as a function of time. An expression for biodegradation is incorporated for those units specifically defined for biodegradation, such as treatment impoundments or wastewater treatment tanks. For these units, the relative rates of air emissions and biodegradation are determined to assess the predicted extent of each mechanism.

The general approach that is used to estimate emissions compares the relative rates of air emissions, biodegradation, and removal with the effluent. Several different types of model units are presented and include mass transfer to the air from quiescent, mechanically aerated, diffused-air, and oil-film liquid surfaces. The other major difference among the types of model units is the type of flow model that is used. For flow-through systems, the degree of mixing can range from complete mixing to plug flow (no mixing), and both cases are presented. For disposal units with no flow out, emissions are a function of time, and average emissions are estimated for some specified time since disposal. The major difference in the emission equations is the liquid-phase concentration that is used for the driving force for mass transfer to the air. The simplest case is represented by well-mixed systems in which the driving force is represented by C_L, the liquid-phase concentration in the bulk liquid, which is also equal to the effluent concentration. Relative removal rates can be compared for this well-mixed case from a simple material balance.

For plug flow, integration is required because the driving force for mass transfer changes as the liquid flows through the system. This concentration is a function of location or time (which are equivalent in plug flow) and is expressed as C_t (denoting a dependence on time). The effluent from a plug flow system is denoted as C_e. For disposal impoundments, the driving-force concentration changes with time and is also denoted as C_t; however, there is no effluent from a disposal impoundment. The integration required for plug flow is from t = 0, when the material first enters the unit, to t = residence time, when the material leaves the unit. For disposal units, the integration is from t = 0, when the material is first placed in the unit, to t = time since disposal, which must be specified to estimate average emissions. The integrated forms of these emission equations are very similar.

The well-mixed flow model is recommended and is the model used in the computer program accompanying this report. This flow model is more generally applicable than plug flow, the calculations are more straightforward, and the two types give similar results. The only exception is a flow-through impoundment with an oil film surface, which uses the plug flow model because the oil film inhibits mixing. Both models yield an estimate of air emissions, biodegradation, and the quantity leaving with the effluent. It is important to recognize that the quantity leaving with the effluent may also eventually contribute to air emissions, especially for treatment units in series or for discharges to streams or publicly owned treatment works.

Equations are presented for estimating the various removal rates, and example calculations for different types of impoundments are also provided. Example calculations are not presented separately for open tanks because the procedure is analogous to that used for impoundments. In general, open tanks will have different input parameters that will account for differences in emission rates compared to impoundments. For example, the liquid surface area for open tanks will be less, and the fetch-to-depth (F/D) ratio will be much lower for tanks. If the open tank has a wind barrier to reduce the wind velocity, the reduced wind velocity can be used in the mass transfer correlations. In addition, the modeling approach accounts for the shorter retention times in tanks (on the order of hours) compared to impoundments (on the order of days). For open tanks, the mass transfer correlation of Springer is recommended for windspeeds less than 3.25 m/s, and the correlation of MacKay and Yeun is recommended for windspeeds greater than 3.25 m/s. Both are discussed in the following section.

4.2 QUIESCENT SURFACES WITH FLOW

4.2.1 Emission Model Equations

The primary focus on emissions from impoundments and wastewater treatment tanks is on aqueous solutions contaminated with organics because aqueous waste is the most common waste type handled in these facilities. For aqueous systems, the basic relationship describing mass transfer of a volatile constituent from the open liquid surface to the air is:

$$E = KAC_L \tag{4-1}$$

where

E = air emissions from the liquid surface, g/s

K = overall mass transfer coefficient, m/s

A = liquid surface area, m^2

C_L = concentration of constituent in the liquid phase, g/m^3.

The overall mass transfer coefficient (K) is estimated from a two-phase resistance model that is based on the liquid-phase mass transfer coefficient (k_L in m/s), the gas-phase mass transfer coefficient (k_G in m/s), and Henry's law constant in the form of a partition coefficient (Keq). The two resistances act in series and the overall resistance is expressed as:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{k_G \, Keq} \qquad (4\text{-}2)$$

where

K = overall mass transfer coefficient, m/s

k_L = liquid-phase mass transfer coefficient, m/s

k_G = gas-phase mass transfer coefficient, m/s

Keq = equilibrium constant or partition coefficient, concentration in gas phase/concentration in liquid phase where both concentrations are in the same units.

Henry's law constant (H in atm•m^3/g mol) is estimated for the constituents of interest by dividing the constituent's vapor pressure (in atmospheres) by its solubility in water (in g mol/m^3). The equilibrium constant is estimated by:

$$Keq = H/RT \qquad (4\text{-}3)$$

where

H = Henry's law constant, atm•m^3/g mol

R = universal gas constant, 8.21×10^{-5} atm•m^3/g mol•K

T = temperature, K.

For a standard temperature of 25 °C, the expression for Keq reduces to:

$$Keq = 40.9 \times H \quad . \qquad (4\text{-}4)$$

The units associated with Keq in Equation (4-4) are the ratio of gas-phase to liquid-phase concentrations and require that both be expressed in the same units of mass/volume.

Several mathematical models have been developed to estimate the individual liquid- and gas-phase mass transfer coefficients. The models are based on different systems, constituents, and sometimes different theoretical considerations. Many of these models yield similar results. The procedures used in this section to estimate the individual mass transfer coefficients rely primarily on existing mass transfer correlations that are believed to be generally applicable.

The liquid-phase mass transfer coefficient (k_L) has been shown to be a function of the constituent's diffusivity in water, windspeed, and liquid depth.[1,2] Work performed at the University of Arkansas by Springer et al.[3] confirmed these effects and resulted in the correlations given in Table 4-1. Springer used simulation studies in a wind tunnel water tank of a constant fetch (2.4 m) and variable depth (4.7 cm to 1.2 m). Fetch is defined as the linear distance across the liquid surface in the direction of the wind flow, and the F/D ratio is defined as the fetch divided by the depth of the impoundment. Ethyl ether was used as the volatile component in the desorption experiments, in which the wind velocity and F/D ratio were varied. Springer's results shown in Table 4-1 yield three different correlations for k_L that depend upon the combination of windspeed and F/D ratio of interest. Springer's model implies that k_L is constant for windspeeds of 0 to 3.25 m/s. Although Springer examined only the mass transfer of ethyl ether, his results are extrapolated to other compounds by the ratio of the compound's and ether's diffusivities in water to the 2/3 power. The windspeed in Springer's correlation is defined as the windspeed 10 m above the liquid surface. For practical application of his correlation, typically reported values of windspeed are used. Springer's model does not include the case in which the F/D ratio is less than 14 and the windspeed is greater than 3.25 m/s. For this specific case, k_L was estimated from MacKay and Yeun's correlation shown in Table 4-1.[7,8] MacKay and Yeun[9] did not address the effect of depth; however, their correlation is based on data from 11 organic compounds in a well-mixed system, the

TABLE 4-1. EQUATIONS FOR CALCULATING INDIVIDUAL MASS TRANSFER COEFFICIENTS FOR VOLATILIZATION OF ORGANIC SOLUTES FROM QUIESCENT SURFACE IMPOUNDMENTS

Liquid phase

Springer et al.[4] (for all cases except $F/D < 14$ and $U_{10} > 3.25$ m/s):

$$k_L = 2.78 \times 10^{-6} \left[\frac{D_w}{D_{ether}}\right]^{2/3} \quad (0 < U_{10} < 3.25)\ (\text{m/s}) \quad (\text{All } F/D \text{ ratios})$$

$$k_L = [2.605 \times 10^{-9}\ (F/D) + 1.277 \times 10^{-7}]\ U_{10}^2 \left[\frac{D_w}{D_{ether}}\right]^{2/3} \quad (U_{10} > 3.25)\ (\text{m/s}) \quad (14 < F/D < 51.2)$$

$$k_L = 2.611 \times 10^{-7}\ U_{10}^2 \left[\frac{D_w}{D_{ether}}\right]^{2/3} \quad (U_{10} > 3.25)\ (\text{m/s}) \quad (F/D > 51.2)$$

where

U_{10} = windspeed at 10 m above the liquid surface, m/s

D_w = diffusivity of constituent in water, cm^2/s

D_{ether} = diffusivity of ether in water, cm^2/s

F/D = fetch-to-depth ratio (fetch is the linear distance across the impoundment).

Gas phase

MacKay and Matasugu (in Hwang[5]):

$$k_G = 4.82 \times 10^{-3}\ U^{0.78}\ Sc_G^{-0.67}\ d_e^{-0.11} \quad (\text{m/s})$$

where

U = windspeed, m/s

Sc_G = Schmidt number on gas side = $\frac{\mu_G}{\rho_G D_a}$

μ_G = viscosity of air, g/cm•s

(continued)

TABLE 4-1 (continued)

ρ_G = density of air, g/cm^3

D_a = diffusivity of constituent in air, cm^2/s

d_e = effective diameter of impoundment = $\left(\frac{4A}{\pi}\right)^{0.5}$, m

A = area of impoundment, m^2.

Liquid phase

MacKay and Yeun[6] (for F/D <14 and U_{10}>3.25 m/s):

$k_L = 1.0 \times 10^{-6} + 34.1 \times 10^{-4}\ U^*\ Sc_L^{-0.5}$ (U^*>0.3) (m/s)

$k_L = 1.0 \times 10^{-6} + 144 \times 10^{-4}\ U^{*2.2} Sc_L^{-0.5}$ (U^*<0.3) (m/s)

where

U^* = friction velocity (m/s) = $0.01\ U_{10}\ (6.1 + 0.63\ U_{10})^{0.5}$

U_{10} = windspeed at 10 m above the liquid surface, m/s

Sc_L = Schmidt number on liquid side = $\frac{\mu_L}{\rho_L D_w}$

μ_L = viscosity of water, g/cm•s

ρ_L = density of water, g/cm^3

D_w = diffusivity of constituent in water, cm^2/s.

compounds represent a broad range of Henry's law constants, and their general correlation is applicable for the case described above that is not covered by Springer's correlation.

The gas-phase coefficient (k_G) was estimated from the correlation of MacKay and Matasugu as shown in Table 4-1.[10] This correlation was developed from experiments on the evaporation of isopropyl benzene, gasoline, and water into air. These researchers verified that previous work, which assumed that the wind velocity profile follows a power law, could be used to quantify the rate of evaporation from a smooth liquid surface. The result was a correlation that expressed k_G as a function of windspeed and the fetch or effective diameter of the liquid surface.

The individual mass transfer coefficients estimated from the correlations in Table 4-1 are used in Equation (4-2) to estimate the overall mass transfer coefficient. The equilibrium constant for a constituent dissolved in water at 25 °C is estimated from Equation (4-4). However, an estimate of the concentration in the liquid phase (C_L) is needed in Equation (4-1) to estimate emissions.

The concentration C_L in Equation (4-1) is the driving force for mass transfer. For an impoundment that is instantly filled with waste, the driving force (C_L) is the initial concentration in the waste. However, this concentration will decrease with time as the constituent is lost to the air, which suggests that emissions may also decrease with time (assuming constant K and A). For flowthrough systems, the concentration may be cyclical if the loading of the process is cyclical. Continuous flowthrough systems may attain some equilibrium concentration.

The flow model assumed for quiescent impoundments and tanks with no biodegradation is that the contents of the system are well mixed and that the bulk concentration (driving force) in the system is equal to the effluent concentration. A material balance around this system yields:

$$QC_o = KAC_L + QC_L \tag{4-5}$$

or

$$C_L = QC_o/(KA+Q) \tag{4-6}$$

where

Q = volumetric flow rate, m^3/s

C_o = initial concentration in the waste, g/m^3

C_L = equilibrium or bulk concentration in the impoundment, g/m^3

K = overall mass transfer coefficient, m/s

A = liquid surface area, m^2.

The well-mixed assumption is made for the sake of simplicity and assumes that bulk convection and wind-induced eddies combine to mix the basin contents. Axial dispersion in the flow direction is also possible, and some systems may be designed specifically for plug flow (e.g., some biological treatment tanks). An assumption of plug flow instead of well-mixed flow would yield slightly higher estimates of emissions; however, the difference is small. Calculations presented by Thibodeaux for an aerated basin that was well-mixed or had plug flow showed that the plug-flow assumption yielded estimates that were higher by 11 percent for acetaldehyde, 5 percent for acetone, and 0 percent for phenol.[11]

The approach described to estimate emissions from quiescent impoundments with no biodegradation includes the following steps:

1. Estimate the individual mass transfer coefficients from Table 4-1.
2. Estimate the equilibrium constant from Equation (4-3).
3. Estimate the overall mass transfer coefficient from Equation (4-2).
4. Estimate the liquid-phase concentration from Equation (4-6).
5. Estimate emissions from Equation (4-1).

The major assumptions associated with this procedure are:

- The two-resistance model and the correlations for the individual mass transfer coefficients are applicable to the system of interest.
- The impoundment's contents are well mixed.
- There is no significant removal by biodegradation, seepage, adsorption, or other forms of degradation.

- The waste material of interest is aqueous waste with no separate organic phase.
- The estimate of Henry's law constant (equilibrium partitioning between the vapor and liquid) is reasonably accurate.

The recommended procedure for quiescent impoundments is to assume that the liquid is well mixed. This assumption is used in the computer model accompanying this report and is illustrated in the example calculations. However, impoundments and tanks with quiescent surfaces can also be designed for plug flow with the use of baffles or other design techniques to reduce the extent of backmixing. In a plug-flow system, the rate of air emissions at any point in the system changes as the material flows through the system. There is no uniform liquid concentration within the plug-flow unit as there was in the well-mixed system, and the lowest concentration occurs in the effluent (i.e., there is no backmixing of the effluent with the influent). For plug flow, the rate of disappearance of a compound by air emissions is given by:

$$\frac{-d\,C_t\,(V)}{dt} = KA\,C_t \tag{4-7}$$

where

C_t = concentration after the plug has traveled t seconds
t = time, s
V = volume, m^3

and with the other symbols as previously defined.

Rearranging Equation (4-7) yields:

$$\frac{d\,C_t}{C_t} = (-KA/V)dt \quad . \tag{4-8}$$

Integrating Equation (4-8) from $C_t = C_o$ at $t = 0$ to $C_t = C_e$ at $t = V/Q$ (one residence time) gives:

$$C_e/C_o = \exp\,(-KA/Q) \tag{4-9}$$

where

C_e = effluent concentration, g/m^3

and with the other symbols as previously defined.

The residence time, τ in seconds, equals V/Q and V = AD (area times depth); consequently, $A/Q = \tau/D$. Substituting into Equation (4-9) yields an equivalent expression:

$$C_e/C_o = \exp(-K\tau/D) \quad . \tag{4-10}$$

The ratio C_e/C_o represents the fraction removed with the effluent; therefore, $1 - C_e/C_o$ represents the fraction that is emitted (f_{air}) from the plug-flow system:

$$f_{air} = 1 - C_e/C_o = 1 - \exp(-K\tau/D) \quad . \tag{4-11}$$

The average emission rate is calculated from:

$$E = f_{air}\, Q\, C_o \tag{4-12}$$

where

E = emissions, g/s

f_{air} = fraction emitted from Equation (4-11)

Q = flow rate, m^3/s

C_o = influent concentration, g/m^3.

4.2.2 Model Plant Parameters for Quiescent Impoundments

A model facility was developed for quiescent impoundments to illustrate the emission estimating procedure. A 1981 survey compiled by Westat[12] showed that the median surface area for storage impoundments was approximately 1,500 m^2 and that the median depth was 1.8 m. Detention times ranged from 1 to 550 days, with over half of the values at 46 days or less. For this example, a detention time of 20 days was chosen. The area and depth yield a total volume of 2,700 m^3, and the detention time of 20 days yields a flow rate of 1.6 L/s (0.0016 m^3/s).

Meteorological conditions are also needed as input parameters for the emission models. For this emission estimate, a standard temperature of 25 °C and a windspeed of 4.47 m/s (10 mi/h) were used. Benzene was chosen as an example constituent at a concentration of 10 g/m^3 (10 ppm) to estimate emissions from the model facility. The properties of benzene that are used include Henry's law constant (5.5×10^{-3} $atm \bullet m^3/g$ mol), diffusivity in air (0.088 cm^2/s), and diffusivity in water (9.8×10^{-6} cm^2/s). Table 4-2 lists the input parameters for the estimate of emissions given in Section 4.2.3.

4.2.3 Example Calculation for Storage Impoundments

This section presents a step-by-step example calculation for emissions from storage impoundments. The equations described in Section 4.2.1 are used with the model unit parameters given in Section 4.2.2 to estimate emissions from an aqueous waste containing 10 g/m^3 of benzene.

a. Calculate liquid-phase mass transfer coefficient, k_L. Use Springer's model (see Table 4-1):

$$\text{Effective diameter} = \left(\frac{\text{Area}}{\pi}\right)^{0.5} \times 2 = \left(\frac{1,500}{\pi}\right)^{0.5} \times 2 = 43.7 \text{ m}$$

$$F/D = \text{Effective diameter/depth} = \frac{43.7}{1.8} = 24.3 .$$

Windspeed = 4.47 m/s ($U_{10} \geq 3.25$ m/s)
F/D = 24.3

$$k_L = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] U_{10}^2 \left(\frac{D_w}{D_{ether}}\right)^{0.67} \text{ m/s}$$

where

U_{10} = windspeed = 4.47 m/s
D_w = 9.8×10^{-6} cm^2/s (benzene)
D_{ether} = 8.5×10^{-6} = cm^2/s (ether)
F/D = 24.3.

Then

$$k_L = [2.605 \times 10^{-9} (24.3) + 1.277 \times 10^{-7}] (4.47)^2 \left(\frac{9.8 \times 10^{-6}}{8.5 \times 10^{-6}}\right)^{0.67}$$

TABLE 4-2. INPUT PARAMETERS--STORAGE IMPOUNDMENT

Area	1,500 m^2
Depth	1.8 m
Volume	2,700 m^3
Retention time	20 days
Flow	0.00156 m^3/s
Temperature	25 °C
Windspeed	4.47 m/s
Constituent	Benzene in water
Concentration	10 g/m^3
Henry's law constant	5.5×10^{-3} atm•m^3/g mol
Diffusivity in air (benzene)	0.088 cm^2/s
Diffusivity in water (benzene)	9.8×10^{-6} cm^2/s
Diffusivity in water (ether)	8.5×10^{-6} cm^2/s
Viscosity of air	1.81×10^{-4} g/cm•s
Density of air	1.2×10^{-3} g/cm^3

$k_L = [2.605 \times 10^{-9} (24.3) + 1.277 \times 10^{-7}] (4.47)^2 (1.1)$

$k_L = 4.2 \times 10^{-6}$ m/s .

b. Calculate gas-phase mass transfer coefficient, k_G. Use MacKay and Matasugu (see Table 4-1):

$$k_G = 4.82 \times 10^{-3}\, U^{0.78}\, Sc_G^{-0.67}\, d_e^{-0.11} (\text{m/s})$$

where

U = windspeed, 4.47 m/s

$$Sc_G = \begin{matrix}\text{Schmidt No.} \\ \text{for gas}\end{matrix} = \frac{\text{viscosity of gas}}{(\text{gas density})(\text{diffusivity of i in gas})}$$

Gas = air

Viscosity (air) = 1.81×10^{-4} g/cm•s

Density (air) = 1.2×10^{-3} g/cm^3

Diffusivity (benzene in air) = 0.088 cm^2/s

$$Sc_G = \frac{1.81 \times 10^{-4} \text{ g/cm•s}}{(1.2 \times 10^{-3} \text{ g/cm}^3)(0.088 \text{ cm}^2\text{/s})} = 1.71$$

d_e = effective diameter = 43.7 m .

Then

$$k_G = (4.82 \times 10^{-3}) (4.47)^{0.78} (1.71)^{-0.67} (43.7)^{-0.11}$$
$$= 7.1 \times 10^{-3} \text{ m/s} .$$

c. Calculate overall mass transfer coefficient (K) from Equation (4-2):

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keq\ k_G}$$

where

$$Keq = \frac{H}{RT} = \frac{5.5 \times 10^{-3} \text{ m}^3\text{•atm/mol}}{(8.21 \times 10^{-5}) \left(\frac{\text{atm•m}^3}{\text{mol•K}}\right) (298 \text{ K})} = 0.225 .$$

Then

$$\frac{1}{K} = \frac{1}{4.2 \times 10^{-6}} + \frac{1}{(0.225)(7.1 \times 10^{-3})} = 2.39 \times 10^{5}$$

$$K = 4.2 \times 10^{-6} \text{ m/s} \quad .$$

d. Estimate emissions for a well-mixed system:

$QC_o = KC_LA + QC_L$ (from material balance of Equation (4-5))

$$C_L = \frac{QC_o}{KA + Q}$$

Detention time = 480 h
Volume = 2,700 m^3

where

$$Q = \text{flow rate} = \left(\frac{2,700 \text{ m}^3}{480 \text{ h}}\right)\left(\frac{1 \text{ h}}{3,600 \text{ s}}\right) = 0.00156 \text{ m}^3\text{/s}$$

$C_o = 10 \text{ g/m}^3$
$K = 4.2 \times 10^{-6}$ m/s

$$C_L = \frac{(0.00156 \text{ m}^3\text{/s})(10 \text{ g/m })^3}{(4.2 \times 10^{-6} \text{ m/s})(1,500 \text{ m}^2) + (0.00156 \text{ m}^3\text{/s})} = 1.98 \text{ g/m}^3$$

$A = 1,500 \text{ m}^2$.

Air emissions = KC_LA (Equation 4-2)

$= (4.2 \times 10^{-6} \text{ m/s})(1.98 \text{ g/m}^3)(1,500 \text{ m}^2) = 0.012$ g/s
$= 0.39$ Mg/yr .

e. Estimate emissions for a plug-flow system:

$f_{air} = 1 - \exp(-K\tau/D)$ (Equation 4-11)

$K = 4.2 \times 10^{-6}$ m/s (Step c)
$\tau = 480 \text{ h} = 1.73 \times 10^{6}$ s
$D = 1.8$ m

$$f_{air} = 1 - \exp\,(-4.2 \times 10^{-6}\ m/s \bullet 1.73 \times 10^{6} s/1.8\ m) = 0.98$$

$$E = f_{air}\ Q\ C_o \text{ (Equation 4-12)}$$

$$f_{air} = 0.98$$
$$Q = 0.00156\ m^3/s$$
$$C_o = 10\ g/m^3$$

$$E = (0.98)(0.00156\ m^3/s)(10\ g/m^3)$$
$$E = 0.015\ g/s = 0.47\ Mg/yr\ .$$

4.3 BIODEGRADATION

This section identifies some of the major design features of biological treatment processes, such as activated sludge units and impoundments designed for biodegradation. Mathematical models for biodegradation are also presented and incorporated into predictive fate models.

4.3.1 Description of Biological Active Systems

The activated sludge process is an aerobic biological treatment in which the pollutants are degraded by microorganisms suspended uniformly in the reaction tank. Oxygen is introduced by mechanical means, and the microorganisms are maintained by recycling the activated sludge that is formed. In most units, the sludge is removed by settling in a separate unit, a portion of the sludge is recycled, and a small portion is wasted (removed from the system) on a continuous basis. Oxidation or stabilization impoundments and aerated impoundments are used to treat entire plant wastes as well as to polish the effluent from other treatment processes. Solids usually settle out in the impoundment or are removed in a separate vessel. Generally, the solids are not recycled; however, if the solids are returned, the process is the same as a modified activated sludge process.[13]

Typical design parameters for an activated sludge process are given in Table 4-3. Two of the most commonly used parameters are the food-to-microorganism (F/M) ratio and residence time. The F/M ratio describes the organic loading on the biological system and is calculated as the weight of BOD_5 (biochemical oxygen demand from a 5-day test) that enters the system in a 24-hour period divided by the total weight of biological solids in the system. The biological solids may be roughly estimated from the mixed

TABLE 4-3. DESIGN PARAMETERS FOR ACTIVATED SLUDGE PROCESSES[14]

Process	F/M,[a] kg BOD/kg biomass•day	Loading, kg BOD/m^3•day	MLSS,[b] g/L	Retention time, h
Conventional[c]	0.2-0.4	0.3-0.6	1.5-3.0	4-8
CSTR[d]	0.2-0.6	0.8-2.0	3.0-6.0	3-5
Contact stabilization	0.2-0.6	1.0-1.2	1.0-3.0[e] 4.0-10[f]	0.5-1[e] 3-6[f]
Extended aeration	0.05-0.15	0.1-0.4	3.0-6.0	18-36
O_2 systems	0.25-1.0	1.6-3.3	6.0-8.0	1-3

[a] F/M = Food to microorganism ratio.

[b] MLSS = Mixed liquor suspended solids.

[c] Plug flow design.

[d] CSTR = Continuous stirred-tank reactor.

[e] Contact unit.

[f] Solids stabilization unit.

liquor suspended solids (MLSS) if substantial quantities of inorganics (such as silt) are not present. If inorganic solids are present, the biological solids may be better approximated by the mixed liquor volatile suspended solids (MLVSS).[15] For municipal wastewater systems, the volatile solids comprise about 60 to 80 percent of the total suspended solids in the sludge; consequently, in the absence of a direct measurement of MLVSS, the biological solids in municipal wastewater can be estimated as 60 to 80 percent of the total suspended solids.[16] Conventional plants, which use an activated sludge process that has long and narrow basins designed to approach plug flow, operate with an F/M ratio of 0.2 to 0.4, but values as low as 0.05 are not unusual. High F/M values indicate a high loading, as from a sudden influx of organics or the loss of biological solids, and will lead to a deterioration in effluent quality.[17]

Aeration tanks are usually constructed of reinforced concrete, are open to the atmosphere, and are usually rectangular in shape. Treatment plants may consist of several tanks, operated in series or parallel. Some of the largest treatment plants may contain 30 to 40 tanks arranged in several groups or batteries.[18]

Typical parameters associated with biologically active impoundments are given in Table 4-4. The loading parameter is expressed in terms of area or volume, and typical retention times in aerated impoundments range from 7 to 20 days. The level of suspended solids in these impoundments is over an order of magnitude less than the level in activated sludge processes. Although the parameters in Table 4-4 are listed as "typical," large variations exist among real facilities, and at a single facility the values may change with time. For example, a study conducted over 12 months at an aerobic impoundment used to treat municipal wastewater reported suspended solids levels of 0.02 to 0.1 g/L and volatile suspended solids of 0.01 to 0.06 g/L.[21] Another study of eight quiescent impoundments at four different sites with confirmed biological activity estimated active biomass concentrations from the rate of oxygen consumption that ranged from 0.0014 to 0.22 g/L with an average of 0.057 g/L.[22]

The biomass concentration is an important parameter in estimating biodegradation rates. The best value to use for a specific site is a

TABLE 4-4. IMPOUNDMENTS DESIGNED FOR BIODEGRADATION[19,20]

Type	Application	Typical daily loading, kg $BOD_5/m^3 \cdot day$	Retention time, d	Typical depth, m	Suspended solids, g/L
Facultative	Raw municipal wastewater Effluent from primary treatment, trickling filters, aerated ponds, or anaerobic ponds	0.0011 - 0.0034[a]	25-180	1.2-2.5	0.11-0.40
Aerated	Industrial wastes Overloaded facultative ponds Situations where limited land area is available	0.008 - 0.32	7-20	2-6	0.26-0.30
Aerobic	Generally used to treat effluent from other processes, produces effluent low in soluble BOD_5 and high in algae solids	0.021 - 0.043[b]	10-40	0.3-0.45	0.14-0.34
Anaerobic	Industrial wastes	0.16 - 0.80	20-50	2.5-5	0.08-0.16

[a] Based on a typical depth of 2 m.

[b] Based on a typical depth of 0.4 m.

direct measurement such as volatile suspended solids for the system of interest. In the absence of site-specific data, a number may be chosen from the ranges for suspended solids given in Tables 4-3 and 4-4. Alternatively, typical or default values for biomass concentration given in Table 4-5 may be used.

The major mechanisms of organic removal in biologically active systems include biodegradation, volatilization, removal with the effluent, and removal by adsorption on the waste sludge. A study by Petrasek et al. of purgeable volatile organics in a pilot-scale wastewater treatment system showed that less than 0.4 percent (generally less than 0.1 percent) of the volatiles were found in the waste-activated sludge.[23] Bishop, in a study of municipal wastewater treatment, concluded that only a modest amount of purgeable toxics were transferred to the sludge.[24] Hannah et al.[25] found that the concentrations of volatile organics in sludges from pilot-scale systems were generally comparable to or less than the corresponding concentrations in the process effluent. This indicated that volatile organics do not have a high affinity for wastewater solids and do not concentrate in the sludges. Kincannon and Stover found that 0 to 1 percent of three compounds (1,2-dichloroethane, phenol, and 1,2-dichlorobenzene) was adsorbed on the sludge.[26] Melcer, in a review of biological removal studies, concluded that polycyclic aromatic hydrocarbons, pyrene, anthracene, fluoranthene, and chrysene were the most commonly occurring priority pollutants found in sludges.[27] These studies suggest that the compounds most likely to be emitted to the air (volatiles) do not concentrate on sludges; however, some of the relatively nonvolatile organics may be adsorbed. Consequently, the modeling approach presented in this section assumes that the removal of volatile organics with the waste sludge is not significant. The major removal mechanisms that are considered include volatilization, biodegradation, and removal with the effluent.

4.3.2 Rate of Biodegradation

Numerous models have been proposed for the removal of organic compounds by biodegradation and include design equations for activated sludge systems and stabilization or oxidation impoundments.[28,29] There is general agreement in the literature that, for high organic loadings relative to

TABLE 4-5. TYPICAL OR DEFAULT VALUES FOR BIOMASS CONCENTRATION[a]

Unit	Biomass concentration (g/L)
Quiescent impoundments	0.05[b]
Aerated impoundments	0.30[c]
Activated sludge units	4.0[d]

[a] These values are recommended for use in the emission equations when site-specific data are not available.

[b] Based on the range (0.0014 to 0.22) and average (0.057) from actual impoundments as discussed in the text.

[c] From the data in Table 4-4 for aerated impoundments. Assumes biomass is approximated by the suspended solids level.

[d] Midrange value from Table 4-3 for CSTR based on mixed liquor suspended solids.

biomass, the biodegradation rate is zero-order with respect to concentration (i.e., the rate is independent of organic concentration). For lower residual levels, the rate becomes first order with respect to concentration or follows Monod-type kinetics.[30,31,32] Data are available from a study by Pitter on the biodegradation of 123 organic compounds and have been expressed as zero-order rate constants.[33] In his experiments, Pitter acclimated the biological medium to the single component of interest. Each compound was evaluated individually by adding the equivalent of about 200 mg/L of chemical oxygen demand (COD) to the system, which contained 100 mg/L of biomass on a dry basis. A blank or control was also run for the single component to verify biological activity and to differentiate between biodegradation and volatilization. Zero-order rate constants for the single component were calculated from the measured biodegradation rate and the rate equation:

$$r = B\ b_i\ V \tag{4-13}$$

where

r = biodegradation rate, g COD/s

B = rate constant, g COD/g biomass/s

b_i = biomass concentration, g/L

V = volume, L.

Pitter's biorate data were converted from grams of COD to grams of the compound based on the theoretical COD of each specific constituent. With this conversion, the rate constant for each compound in the data base derived from Pitter's data was expressed as g compound/g biomass•s. Although Pitter's study provides the primary source of the biodegradation rate constants, data on additional compounds were obtained from Kincannon and Stover.[34] The biodegradation rate constant was calculated directly from Equation (4-13) based on the reported rate of disappearance of the compound. The rate given by Equation (4-13) and calculated by Pitter represents a maximum biodegradation rate for the pure component that is independent of the compound's concentration. This represents the case in which there is an excess of food for the microorganisms. However, as the organic concentration or available food decreases, the rate becomes first order, and the biodegradation rate decreases from the maximum rate as the compound's concentration decreases.

The design equations for activated sludge systems and stabilization ponds are based on the type of flow (usually either plug flow or well-mixed flow) and the rate expression for the biodegradation reaction. Numerous models have been proposed for the biodegradation rate (applicable to either plug or well-mixed flow) and include:

McKinney:[35] $r = B_1 V C_L$ (4-14)

Eckenfelder(1):[36] $r = B_2 b_i V C_L$ (4-15)

Eckenfelder(2):[37] $r = B_3 b_i V C_L/C_o$ (4-16)

where

r = biodegradation rate, g/s

B_1, B_2, B_3 = rate constants

V = volume, L

b_i = biomass concentration, g/L

C_L = effluent concentration (also equals bulk liquid concentration for well-mixed flow), g/L

C_o = influent concentration, g/L .

The rate expressions in Equations (4-14), (4-15), and (4-16) are among the simplest found in the literature. More complex expressions are provided by Gaudy, Lawrence, and McCarty, and Kincannon and Stover;[38] however, these models require knowledge of additional system parameters and are difficult to use in the generic modeling approach presented here. In addition, the data base for biodegradation of specific compounds is very limited. A zero-order data base is available based on Pitter's measurements; consequently, a modeling approach is needed that either permits the use of Pitter's data to examine the biodegradation rate of specific compounds or is compatible with another data base.

Eckenfelder reported that the removal of a single component by biodegradation exhibited zero-order kinetics to low residual levels. With mixtures of organics, concurrent removal occurs at different rates, which depend on the organic in question. For the overall rate of removal, he described the rate in Equation (4-16) as proportional to the fraction of organics remaining in the basin. Because the more readily degradable organics will be removed first, he stated that the apparent rate of the overall reaction must decrease with increasing removals.[39] For organic loadings that are much higher than the biodegradation capacity, C_L in Equation (4-16) will approach the value of C_O. In this case, Equation (4-16) reduces to $r = K_3 b_i V$, which is equivalent to the zero-order rate expression used by Pitter to derive the rate constants for specific organic compounds. However, as the organic concentration in the system (C_L) decreases, Equation (4-16) predicts that the biodegradation rate will also decrease, whereas Pitter's rate model would assume that biodegradation would still occur at the maximum rate. Consequently, Eckenfelder's rate expression in Equation (4-16) will be incorporated into the modeling approach to provide an estimate based on first-order biodegradation rates for low concentrations of organics.

The biodegradation rate and air emission rate can be incorporated into a material balance to determine the relative extent of each mechanism. For a well-mixed unit, the bulk liquid concentration is uniform and is equal to the effluent concentration. A material balance yields:

$$Q\,C_o = Q\,C_L + B\,b_i\,V\,C_L/C_o + K\,A\,C_L \qquad (4\text{-}17)$$

where

Q = flow rate, m^3/s
C_O = inlet concentration, g/m^3
C_L = bulk liquid and effluent concentration, g/m^3
B = biorate constant, g/s per g biomass
b_i = biomass concentration, g/m^3
V = volume, m^3
K = overall mass transfer coefficient, m/s
A = area, m^2 .

The material balance in Equation (4-17) is for a system with biodegradation and assumes that: (1) the flow system is operated at steady-state conditions, (2) C_L is always less than C_O, (3) there is no excess food because the biomass concentration is sufficiently high, and (4) first-order biodegradation applies and the zero-order regime is never entered.

The fraction emitted to the air (f_{air}) is:

$$f_{air} = K\ A\ C_L/Q\ C_o\ . \tag{4-18}$$

Substituting Equation (4-17) into Equation (4-18) and rearranging yields:

$$f_{air} = KA/(Q + B\ b_i V/C_o + KA)\ . \tag{4-19}$$

Emissions (E, g/s) are calculated from:

$$E = f_{air}\ QC_o\ . \tag{4-20}$$

Similarly, the fraction biodegraded (f_{bio}) is:

$$f_{bio} = (B\ b_i V/C_o)/(Q + B\ b_i\ V/C_o + KA)\ . \tag{4-21}$$

The effluent concentration from Equation (4-17) is:

$$C_L = Q\ C_o/(Q + Bb_i V/C_o + KA)\ . \tag{4-22}$$

If the biological system is operated with plug flow, the treated wastewater does not mix with the influent. The biodegradation rate and air emission rate change as the treatment progresses toward completion. For plug flow, the rate of disappearance of a compound by biodegradation and air emissions is given by:

$$\frac{-d\ C_t\ (V)}{dt} = B\ b_i\ V\ C_t/C_o + KA\ C_t \tag{4-23}$$

where

C_t = concentration at time = t
t = time, s

and with the other symbols as previously defined. Rearranging Equation (4-23) yields:

$$\frac{d\ C_t}{C_t} = (-B\ b_i/C_o - KA/V)\ dt\ . \tag{4-24}$$

Integrating Equation (4-24) from $C_t = C_o$ at $t = 0$ to $C_t = C_e$ (effluent concentration) at $t = V/Q$ (one residence time) gives:

$$C_e/C_o = \exp\left(-B\, b_i V/QC_o - KA/Q\right) \quad . \tag{4-25}$$

The ratio C_e/C_o represents the fraction leaving with the effluent; consequently, $1 - C_e/C_o$ represents the sum of the fractions that are biodegraded and emitted to the air. The fractions emitted to the air and biodegraded are calculated from their relative rates:

$$f_{air} = (1 - C_e/C_o)(KA)/(KA + B\, b_i V/C_o) \tag{4-26}$$

$$f_{bio} = (1 - C_e/C_o)(B\, b_i V/C_o)/(KA + B\, b_i V/C_o) \quad . \tag{4-27}$$

Equations (4-19) and (4-26) provide estimates of the fraction of a component entering the system that is emitted to the air for well-mixed and plug-flow systems, respectively. This approach assumes that the entire active biomass is degrading only the constituent of interest; however, real systems contain multiple components that will degrade at different rates.

Biological systems are limited in their rate of consumption of biodegradable volatile organics. If only one compound is present as a food source in the loading on the system, the rate of consumption can approach the maximum zero-order rate for that compound. However, if multiple compounds are present, the limited amount of biomass available cannot biologically degrade all of the compounds at the sum of their maximum rates. The biodegradation rate for a single compound in a mixture of compounds must be reduced to account for the competition for biooxidation mechanisms from all of the compounds. The rate of consumption of a single compound in a mixture is reduced by multiplying its maximum individual rate by a weighting factor (W). For component 1 in a mixture of n components, the weighting factor is defined as:

$$W_1 = B_1\, C_{01} \left[\sum_{i=1}^{n} B_i C_{oi} \right]^{-1} \tag{4-28}$$

where

W_1 = weighting factor for component 1, dimensionless fraction

B_1 = biorate for component 1, g/s per g biomass

Co_1 = inlet concentration of component 1, g/m^3

n = number of components in the mixture
B_i = biorate of component i, g/s per g biomass
Co_i = inlet concentration of component i, g/m^3.

For a single component system, Equation (4-28) reduces to $W_1 = 1$. The weighting factor is multiplied by the pure component biorate (B) to determine the compound's effective biorate in a multicomponent mixture. For mixtures, B is replaced in Equations (4-19) and (4-26) by W_1B_1 to estimate the fraction of component 1 emitted to the air.

For mixtures, the first choice for the overall biorate is a direct measurement in a closed system that is based on BOD or COD removal. However, these data are often not available for specific systems. An alternative approach is to identify each constituent and its biorate to use in Equation (4-28). If neither an overall rate nor specific constituents are available, the use of a default value is recommended. For example, the biorate of a relatively biodegradable compound (such as 5.28×10^{-6} g/s/g biomass for benzene) should be a reasonable approximation for the biorate of the entire mixture.

4.3.3 Example Calculation for Quiescent Impoundments

The application of the biodegradation model to quiescent impoundments is presented in the form of an example calculation. The calculation is based on the quiescent impoundment's operating parameters from Table 4-2. For other types of impoundments, the application of the biodegradation model is illustrated in subsequent sections.

The waste stream for the example calculation is defined as containing benzene at 10 ppm with a total organic content of 250 ppm (0.25 g/L). The resultant organic loading on the impoundment on a daily basis is 12.8 kg/1,000 m^3. The active biomass is assumed to be 0.05 g/L from a reported range from eight quiescent impoundments of 0.0014 to 0.22 g/L. The biorate for benzene is 5.28×10^{-6} g/s/g biomass, and it is assumed that the other organic components degrade at approximately the same rate.

a. Calculate the weighting factor to account for the competition for available biomass from Equation (4-28). Because the biorates for benzene and the mixture are assumed to be equal, Equation (4-28) reduces to the ratio of concentrations 10/250 = 0.04. The effective biorate for benzene in the mixture is $(0.04)(5.28 \times 10^{-6}$ g/s/g biomass$) = 2.1 \times 10^{-7}$ g/s/g biomass.

b. Calculate the fraction emitted for a well-mixed system from Equation (4-19):

$$f_{air} = KA/(Q + B\ b_iV/C_o + KA)$$

where

$K = 4.2 \times 10^{-6}$ m/s (Section 4.2.3, Step c)

$A = 1{,}500\ m^2$

$Q = 0.00156\ m^3/s$

$B = 2.1 \times 10^{-7}$ g/s/g biomass

$b_i = 0.05\ g/L = 50\ g/m^3$

$V = 2{,}700\ m^3$

$C_o = 10\ ppm = 10\ g/m^3$

$$KA = (4.2 \times 10^{-6}\ m/s)(1{,}500\ m^2) = 6.3 \times 10^{-3}\ m^3/s$$

$$B\ b_iV/C_o = (2.1 \times 10^{-7}\ g/s/g\ biomass)(50\ g/m^3)(2{,}700\ m^3)/10\ g/m^3$$

$$= 2.84 \times 10^{-3}\ m^3/s$$

$$f_{air} = 6.3 \times 10^{-3}\ m^3/s/(0.00156\ m^3/s + 2.84 \times 10^{-3}\ m^3/s + 6.3 \times 10^{-3}\ m^3/s)$$

$$f_{air} = 0.589\ .$$

c. Calculate benzene emissions for well-mixed system:

$$E(g/s) = f_{air}\ Q\ C_o$$

$$= (0.589)(0.00156\ m^3/s)(10\ g/m^3)$$

$$= 9.2 \times 10^{-3}\ g/s = 0.29\ Mg/yr\ .$$

d: For a plug-flow system, calculate fraction removed with the effluent from Equation (4-25):

$$C_e/C_o = \exp\ (-\ B\ b_i\ V/Q\ C_o - KA/Q)$$

where

$B = 2.1 \times 10^{-7}$ g/s/g biomass

$b_i = 0.05\ g/L = 50\ g/m^3$

$V = 2{,}700\ m^3$

$Q = 0.00156\ m^3/s$

$C_o = 10\ ppm = 10\ g/m^3$

$K = 4.2 \times 10^{-6}$ m/s

$A = 1{,}500\ m^2$

$$B\ b_i\ V = (2.1 \times 10^{-7}\ \text{g/s/g biomass})(50\ \text{g/m}^3)(2{,}700\ \text{m}^3)$$
$$= 2.84 \times 10^{-2}\ \text{g/s}$$
$$Q\ C_o = (0.00156\ \text{m}^3/\text{s})(10\ \text{g/m}^3) = 1.56 \times 10^{-2}\ \text{g/s}$$
$$KA = (4.2 \times 10^{-6}\ \text{m/s})(1{,}500\ \text{m}^2) = 6.3 \times 10^{-3}\ \text{m}^3/\text{s}$$

$$C_e/C_o = \exp\left[\frac{-2.84 \times 10^{-2}\ \text{g/s}}{1.56 \times 10^{-2}\ \text{g/s}} - \frac{6.3 \times 10^{-3}\ \text{m}^3/\text{s}}{1.56 \times 10^{-3}\ \text{m}^3/\text{s}}\right]$$
$$C_e/C_o = \exp(-5.86) = 2.85 \times 10^{-3}\ .$$

e. Calculate fraction emitted from Equation (4-26):

$$f_{air} = (1 - C_e/C_o)(KA)/(KA + B\ b_i\ V/C_o)$$
$$f_{air} = (1 - 2.85 \times 10^{-3})(6.3 \times 10^{-3}\ \text{m}^3/\text{s}) / (6.3 \times 10^{-3}\ \text{m}^3/\text{s} + 2.84 \times 10^{-2}\ \text{g/s}/10\ \text{g/m}^3)$$
$$f_{air} = 0.687\ .$$

f. Calculate benzene emissions for plug flow:

$$E(\text{g/s}) = f_{air}\ Q\ C_o$$
$$= (0.687)(0.00156\ \text{m}^3/\text{s})(10\ \text{g/m}^3)$$
$$= 1.07 \times 10^{-2}\ \text{g/s} = 0.34\ \text{Mg/yr}\ .$$

4.4 MECHANICALLY AERATED IMPOUNDMENTS AND ACTIVATED SLUDGE UNITS

Some impoundments and tanks are mechanically agitated to improve mixing or to transfer air to the liquid (e.g., treatment tanks designed for biodegradation). The agitation creates a turbulent liquid surface that enhances mass transfer to the air. A significant difference from the approach for quiescent surfaces discussed in Section 4.2 is the appropriate correlations for the individual mass transfer coefficients.

4.4.1 Emission Model Equations

The calculation of the overall mass transfer coefficient for mechanically aerated systems considers that the liquid surface is composed of two zones, quiescent and turbulent. The individual mass transfer coefficients for the turbulent zone are based on the correlations of Thibodeaux[40] and Reinhardt.[41] Thibodeaux's model was developed from accepted interphase mass transfer concepts, published rate coefficient correlations, and existing operating data on 13 aerated basins at 11 pulp and paper mills. The basins represented a wide range of design and operating parameters, in spite of being from only one industry type. The simulation employed 11 organic chemical species common to industrial wastewater.

Reinhardt absorbed ammonia in aqueous sulfuric acid to measure the gas-phase mass transfer coefficient associated with flat-blade surface agitators in developing his correlation to calculate the gas-phase mass transfer coefficient.[42]

Table 4-6 summarizes the correlations developed by Thibodeaux and Reinhardt. These correlations are used to estimate the individual mass transfer coefficients for the turbulent portion of the liquid surface. The individual coefficients are then used in Equation (4-2) to calculate an overall mass transfer coefficient for the turbulent zone. An overall mass transfer coefficient for the quiescent zone is calculated as described in Section 4.2. The two overall coefficients are combined to obtain a single coefficient for the system based on the relative areas of the turbulent and quiescent zones. For example, if 25 percent of the surface of the impoundment is turbulent, the overall coefficient would be the sum of 25 percent of the value for the turbulent area coefficient plus 75 percent of the value for the quiescent zone.

The model for mechanically aerated systems also incorporates biodegradation as a competing mechanism. The extent of biodegradation is difficult to predict in a generally applicable form because it is very dependent upon the constituent of interest, the waste matrix, the design and operation of the biodegradation unit, and the concentrations and properties of the microorganisms Field studies are currently under way to assess the relative extent of air emissions and biodegradation. These studies should provide insight into the reasonableness of the modeling approach described in this section.

4.4.2 Model Plant Parameters for Mechanically Aerated Impoundments

The dimensions of the treatment impoundment used as an example to estimate emissions were derived from the Westat data as described in Section 4.2.2 for storage impoundment. A median area of 1,500 m^2 and a depth of 1.8 m were chosen, which yields a total volume of 2,700 m^3. The retention time in treatment impoundments is expected to be less than the

TABLE 4-6. EQUATIONS FOR CALCULATING INDIVIDUAL MASS TRANSFER COEFFICIENTS FOR VOLATILIZATION OF ORGANIC SOLUTES FROM TURBULENT SURFACE IMPOUNDMENTS

Liquid phase

Thibodeaux:[43,44]

$$k_L = [8.22 \times 10^{-9}\ J\ (POWR)(1.024)^{t-20}\ O_t\ 10^6\ MW_L/(Va_v\rho_L)]\ (D_w/D_{O_2,w})^{0.5}\ (m/s)$$

where

J = oxygen transfer rating of surface aerator, lb O_2/h•hp

POWR = total power to aerators, hp

T = water temperature, °C

O_t = oxygen transfer correction factor

MW_L = molecular weight of liquid

V = volume affected by aeration, ft^3

a_v = surface-to-volume ratio of surface impoundment, ft^{-1}

ρ_L = density of liquid, g/cm^3

D_w = diffusivity of constituent in water, cm^2/s

$D_{O_2,w}$ = diffusivity of oxygen in water = 2.4×10^{-5}, cm^2/s.

Gas phase

Reinhardt:[45,46]

$$k_G = 1.35 \times 10^{-7}\ R_e^{1.42}\ p^{0.4}\ Sc_G^{0.5}\ F_r^{-0.21}\ D_a MW_a/d\ (m/s)$$

where

$R_e = d^2 w \rho_a/\mu_a$ = Reynold's number

d = impeller diameter, cm

w = rotational speed of impeller, rad/s

(continued)

TABLE 4-6 (continued)

ρ_a = density of air, g/cm^3

μ_a = viscosity of air, g/cm•s

= 4.568×10^{-7} T(°C) + 1.7209×10^{-4}

p = $P_I \, g_c/(\rho_L d^{*5} w^3)$ = power number

P_I = power to impeller, ft•lb_f/s

= 0.85 (POWR) (550 ft•lb_f/s•hp)/number of aerators,

where 0.85 = efficiency of aerator motor

g_c = gravitation constant, 32.17 lb_m•ft/s^2/lb_f

ρ_L = density of liquid, lb/ft^3

d* = impeller diameter, ft

Sc_G = Schmidt number on gas side = $\mu_a/\rho_a D_a$

F_r = d^*w^2/g_c = Froude number

D_a = diffusivity of constituent in air, cm^2/s

MW_a = molecular weight of air.

retention time in storage impoundments. Two design manuals listed typical retention times for aerated (biologically active) ponds as 7 to 20 days[47] and 3 to 10 days.[48] For the example case, a retention time of 10 days was chosen from the design range of 3 to 20 days. The resulting flow rate is 3.1 L/s (0.0031 m^3/s).

The correlations of Thibodeaux and Reinhardt given in Table 4-3 require values for the parameters that describe the mechanical aeration system. Metcalf and Eddy, Inc.,[49] suggest a range of 0.5 to 1.0 hp/1,000 ft^3 for mixing in an impoundment. However, more power may be needed to supply additional oxygen or to mix certain treatment solutions. A review of trip reports showed power usage as high as 3.5 hp/1,000 ft^3 at a specific TSDF impoundment.[50] For this analysis, a midrange value of 0.75 hp/1,000 ft^3 from Metcalf and Eddy was used to generate an estimate of 75 hp required for mixing in the model unit.

Data from Reference 51 indicated that an aerator with a 75-hp motor and a 61-cm diameter propeller turning at 126 rad/s would agitate a volume of 658 m^3 (23,240 ft^3). Assuming a uniform depth in the impoundment of 1.8 m, the agitated surface area was estimated as 366 m^2 (658/1.8). The agitated surface is assumed to be turbulent and comprises 24 percent (366/1,500 x 100) of the total area. The balance of the surface area of the impoundment (76 percent) is assumed to be quiescent. As a comparison, Thibodeaux reported a turbulent area of 5.22 m^2/hp and investigated a range of 0.11 to 20.2 m^2/hp. The value of 5.22 m^2/hp and a total of 75 hp yields an estimated turbulent area of 392 m^2 (26 percent), which compares favorably with the 24-percent turbulent area calculated by the alternative approach.[52] (Very few data are available on the distribution of turbulent areas for aerated impoundments. The extent of turbulence depends in part on the number, size, and placement of aerators. The example is based on typical aerator requirements to mix the contents of the impoundment.)

Typical values were chosen for the oxygen transfer rating of the aerator and the oxygen transfer correction factor. A value of 3.0 lb O_2/hp/h was chosen for oxygen transfer rating from a range of 2.9 to 3.0.[53] A value of 0.83 was used for the correction factor from a typical range of

0.80 to 0.85.[54] The transfer of power to the impeller was assumed to be 85 percent efficient, yielding an estimate of 64 hp for the impeller power.

The model for biodegradation requires the system's biomass concentration as an input parameter. The concentration of biomass in real systems can be highly variable depending upon the system's design and method of operation. For this analysis, the specified biomass is assumed to be actively degrading the constituent of interest. A value of 300 g/m^3 (0.3 g/L) of biomass was chosen from the values presented in Table 4-5.

The example constituent (benzene) and the meteorological conditions chosen for the example calculation are the same as those chosen for storage impoundments. Input parameters for the mechanically aerated model unit are summarized in Table 4-7.

4.4.3 Example Calculation for Mechanically Aerated Treatment Impoundments

The example calcuiation for emissions from a mechanically aerated impoundment includes an estimate of the overall mass transfer coefficient for the turbulent zone. The overall mass transfer coefficient for the quiescent zone for storage impoundments is calculated as illustrated in Section 4.2.3 and will not be repeated here. Biodegradation is included as a competing removal mechanism.

a. Calculate turbulent liquid-phase mass transfer coefficient, k_L. Use Thibodeaux (Table 4-6):

$$k_L(\mathrm{m/s}) = [8.22 \times 10^{-9}\ J(\mathrm{POWR})(1.024)^{T-20}\ O_t\ 10^6\ MW_L/(Va_v \rho_L)] \left[\frac{D_w}{D_{O_2,w}}\right]^{0.5}$$

where

J = O_2 transfer rating, use 3.0 lb O_2/h•hp

POWR = 75 hp

T = water temperature = 25 °C

O_t = O_2 transfer correction factor, use 0.83

MW_L = molecular wt of liquid (water) = 18 g/g mol

$$(Va_v) = \text{agitated area in ft}^2 = 366.0\ \mathrm{m}^2 \left[\frac{\mathrm{ft}^2}{0.0929\ \mathrm{m}^2}\right] = 3{,}940\ \mathrm{ft}^2$$

TABLE 4-7. INPUT PARAMETERS--TREATMENT IMPOUNDMENTS
(MECHANICALLY AERATED)

Area: 1,500 m^2

Depth: 1.8 m

Volume: 2,700 m^3

Retention time: 10 days

Flow: 0.0031 m^3/s

Turbulent area: 366 m^2 (24%)

Quiescent area: 1,134 m^2

Total power: 75 hp

Power to impeller: 64 hp

Impeller speed: 126 rad/s

Impeller diameter: 61 cm

O_2 transfer: 3 lb/h/hp

O_2 correction factor: 0.83

Temperature: 25 °C

Windspeed: 4.47 m/s

Viscosity of air: 1.8×10^{-4} g/cm•s

Density of air: 1.2×10^{-3} g/cm^3

Diffusivity of O_2 in water: 2.4×10^{-5} cm^2/s

Density of liquid: 1 g/cm^3

Molecular weight of liquid: 18 g/g•mol

Molecular weight of air: 29 g/g•mol

Constituent: benzene with other biodegradable organics in water

Concentration (benzene): 10 g/m^3 (10 ppm)

Concentration (total organics): 250 g/m^3 (250 ppm)

Henry's law constant (benzene): 5.5×10^{-3} atm•m^3/g mol

(continued)

TABLE 4-7 (continued)

Diffusivity in air (benzene): 0.088 cm^2/s

Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s

Biorate (benzene and other organics): 19 mg/h/g of biomass =

5.28×10^{-6} g/g biomass•s

Biomass concentration: 0.3 g/L = 300 g/m^3

ρ_L = water density = 1 g/cm^3

D_w = 9.8 x 10^{-6} cm^2/s

$D_{O_2,w}$ = 2.4 x 10^{-5} cm^2/s

$$k_L = (8.22 \times 10^{-9})(3)(75)(1.024)^5 \left[\frac{(0.83)(10^6)(18)}{(3,940)\ (1)}\right] \left[\frac{9.8 \times 10^{-6}}{2.4 \times 10^{-5}}\right]^{0.5}$$

$$= 5.0 \times 10^{-3} \text{ m/s} \quad .$$

b. Calculate turbulent gas-phase mass transfer coefficient, k_G. Use Reinhardt (see Table 4-6):

$$k_G(\text{m/s}) = 1.35 \times 10^{-7}\ Re^{1.42}\ p^{0.4}\ Sc_G^{0.5}\ Fr^{-0.21}\ D_a\ MW_a/d$$

where

Re = Reynold's number = $\frac{d^2 w\ \rho_a}{\mu_a}$

d = impeller diameter = 61 cm

w = impeller speed = 126 rad/s

ρ_a = 1.2 x 10^{-3} g/cm^3

μ_a = 1.81 x 10^{-4} g/cm•s

$$Re = \frac{(61^2)\ (126)\ (1.2 \times 10^{-3})}{1.81 \times 10^{-4}} = 3.1 \times 10^6$$

p = power number = $\frac{P_I\ g_c}{\rho_L d^{*5} w^3}$

$$P_I = 64 \text{ hp } \frac{550 \text{ ft lb}_f}{\text{s}\bullet\text{hp}} = 35,200$$

$$g_c = 32.17 \ \frac{\text{lb}\bullet\text{ft}}{\text{s} \ \ \text{lb}_f^2}$$

ρ_L = 62.37 lb/ft^3

d* = impeller diameter in feet = 2.0

w = 126 rad/s

$$p = \frac{(35{,}200)\ \ (32.17)}{(62.37)(2^5)(126)^3} = 2.8 \times 10^{-4}$$

Sc_G = 1.71 (from Section 4.2.3, part b)

$$Fr = \text{Froude number} = \frac{d^* w^2}{g_c} = \frac{(2)(126)^2}{32.17} = 9.9 \times 10^2$$

D_a = 0.088 cm^2/s (benzene)

MW_a = 29 g/g mol

d = impeller diameter in cm = 61 cm

$$k_G = (1.35\text{x}10^{-7})(3.1\text{x}10^6)^{1.42}\ (2.8\text{x}10^{-4})^{0.4}(1.71)^{0.5}(9.9\text{x}10^2)^{-0.21}$$
$$(0.088)(29)/61$$

$k_G = 1.1 \times 10^{-1}$ m/s .

c. Calculate overall mass transfer coefficient for turbulent area, K:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keq\ k_G} = \frac{1}{5.0 \times 10^{-3}} + \frac{1}{(0.225)(1.1 \times 10^{-1})} = 2.4 \times 10^2$$

$K = 4.2 \times 10^{-3}$ m/s .

d. Calculate overall mass transfer coefficient for combined quiescent and turbulent areas, K:

From Section 4.2.3, K for quiescent area = 4.2×10^{-6} m/s

From Part C, K for turbulent area = 4.2×10^{-3} m/s

Turbulent area = 366 m^2

Quiescent area = 1,134 m^2

$$K\ (\mathrm{m/s})\ \text{(weighted by area)} = \frac{(4.2 \times 10^{-6})(1{,}134)+(4.2 \times 10^{-3})(366)}{(1{,}134 + 366)} = 1.0 \times 10^{-3}\ \mathrm{m/s}\ .$$

e. Calculate the weighting factor to account for the competition for available biomass from Equation (4-28). Because the biorates for benzene and the mixture are assumed to be equal, Equation (4-28) reduces to the ratio of concentrations 10/250 = 0.04. The effective biorate for benzene in the mixture is $(0.04)(5.28 \times 10^{-6}$ g/s/g biomass) = 2.1×10^{-7} g/s/g biomass.

f. Calculate the fraction emitted for a well-mixed system from Equation (4-19):

$$f_{air} = KA/(Q + B\ b_i\ V/C_o + KA)$$

where

$K = 1.0 \times 10^{-3}$ m/s

$A = 1{,}500\ \mathrm{m}^2$

$Q = 0.0031\ \mathrm{m}^3/\mathrm{s}$

$B = 2.1 \times 10^{-7}$ g/s/g biomass

$b_i = 0.3\ \mathrm{g/L} = 300\ \mathrm{g/m}^3$

$V = 2{,}700\ \mathrm{m}^3$

$C_o = 10\ \mathrm{ppm} = 10\ \mathrm{g/m}^3$

$$KA = (1.0 \times 10^{-3}\ \mathrm{m/s})(1{,}500\ \mathrm{m}^2) = 1.5\ \mathrm{m}^3/\mathrm{s}$$

$$B\ b_i\ V/C_o = (2.1 \times 10^{-7}\ \mathrm{g/s/g\ biomass})(300\ \mathrm{g/m}^3)(2{,}700\ \mathrm{m}^3)/10\ \mathrm{g/m}^3$$

$$= 1.7 \times 10^{-2}\ \mathrm{m}^3/\mathrm{s}$$

$$f_{air} = 1.5\ \mathrm{m}^3/\mathrm{s}/(0.0031\ \mathrm{m}^3/\mathrm{s} + 0.017\ \mathrm{m}^3/\mathrm{s} + 1.5\ \mathrm{m}^3/\mathrm{s})$$

$$f_{air} = 0.987\ .$$

g. Calculate benzene emissions for well-mixed system:

$$E(\mathrm{g/s}) = f_{air}\ Q\ C_o$$

$$= (0.987)(0.0031\ \mathrm{m}^3/\mathrm{s})(10\ \mathrm{g/m}^3)$$

$$= 3.06 \times 10^{-2}\ \mathrm{g/s} = 0.97\ \mathrm{Mg/yr}\ .$$

h. For a plug-flow system, calculate the fraction removed with the effluent from Equation (4-25):

$$C_e/C_o = \exp(-B\ b_i\ V/Q\ C_o - KA/Q)$$

$B = 2.1 \times 10^{-7}$ g/s/g biomass (effective biorate from Step e)

$b_i = 0.3$ g/L = 300 g/m^3

$V = 2{,}700$ m^3

$Q = 0.0031$ m^3/s

$C_o = 10$ ppm = 10 g/m^3

$K = 1.0 \times 10^{-3}$ m/s

$A = 1{,}500$ m^2

$$B\ b_i\ V = (2.1 \times 10^{-7}\ \text{g/s/g biomass})(300\ \text{g/m}^3)(2{,}700\ \text{m}^3)$$
$$= 0.17\ \text{g/s}$$

$$Q\ C_o = (0.0031\ \text{m}^3/\text{s})(10\ \text{g/m}^3) = 0.031\ \text{g/s}$$

$$KA = (1.0 \times 10^{-3}\ \text{m/s})(1{,}500\ \text{m}^2) = 1.5\ \text{m}^3/\text{s}$$

$$C_e/C_o = \exp\left(\frac{-0.17\ \text{g/s}}{0.031\ \text{g/s}} - \frac{1.5\ \text{m}^3/\text{s}}{0.0031\ \text{m}^3/\text{s}}\right) = 0\ .$$

i. Calculate fraction emitted from Equation (4-26):

$$f_{air} = (1 - C_e/C_o)(KA)/(KA + B\ b_i\ V/C_o)$$

$$f_{air} = (1 - 0)(1.5\ \text{m}^3/\text{s})/(1.5\ \text{m}^3/\text{s} + 0.17\ \text{g/s}/10\ \text{g/m}^3)$$

$$f_{air} = 0.989\ .$$

j. Calculate benzene emissions for plug flow:

$$E(\text{g/s}) = f_{air}\ Q\ C_o$$
$$= (0.989)(0.0031\ \text{m}^3/\text{s})(10\ \text{g/m}^3)$$
$$= 3.07 \times 10^{-2}\ \text{g/s} = 0.97\ \text{Mg/yr}\ .$$

4.4.4 Example Calculation for Activated Sludge Unit

As discussed in Section 4.2, an activated sludge unit usually consists of a concrete tank that is aerated and contains a relatively high concentration of active biomass. A model unit is defined in this section for this process, and the results of intermediate and final calculations are given. Detailed example calculations are not presented because the approach is exactly the same as that used for the mechanically aerated impoundment. The only significant difference in the method of operation is the recycle of solids back to the activated sludge unit, which results in a higher biomass concentration. For this model unit, a biomass concentration of 4 g/L (4,000 g/m^3) was chosen from the range of 1.5 to 6 g/L in Table 4-3 and the recommended values in Table 4-5. Other differences between the aerated impoundment and activated sludge tank include, for the tank, a smaller surface area, a shorter retenticn time, a greater turbulent area, and a smaller F/D ratio. The aerated surface area was estimated as described in Section 4.4.2. An aerator with a 7.5-hp motor will agitate a volume of 56.9 m^3 (2,010 ft^3). For a uniform depth of 4 m, the agitated volume yields an agitated surface area of 14.2 m^2 (56.9 m^3/4 m). The input parameters are defined for this model unit in Table 4-8, and the results of the calculations are presented in Table 4-9.

4.5 DISPOSAL IMPOUNDMENTS WITH QUIESCENT SURFACES

4.5.1 Emission Model Equations

A disposal impoundment is defined as a unit that receives a waste for ultimate disposal rather than for storage or treatment. This type of impoundment differs from the storage and treatment impoundments in that there is no liquid flow out of the impoundment (seepage into the ground is neglected). For this case, the well-mixed system with a bulk concentration that is at equilibrium (i.e., the bulk concentration does not change with time) is not applicable. The quantity of a constituent in a disposal impoundment will decrease with time after the waste is placed in the impoundment because of the loss of volatiles to the air.

The calculation of the overall mass transfer coefficient is the same as that presented for impoundments with quiescent surfaces. If the disposal impoundment is aerated, K is calculated as described for aerated impoundments in Section 4.4. The emission estimating procedure differs in the calculation of the liquid-phase concentration that is the driving force for mass transfer to the air. For a disposal impoundment that is filled with a batch of waste, the rate of disappearance of a compound by biodegradation and air emissions is:

TABLE 4-8. INPUT PARAMETERS--MECHANICALLY AERATED ACTIVATED SLUDGE UNIT

Area: 27 m^2
Depth: 4 m
Volume: 108 m^3
Retention time: 4 h
Flow: 0.0075 m^3/s
Turbulent area: 14.2 m^2 (53%)
Quiescent area: 12.8 m^2

Total power: 7.5 hp
Power to impeller: 6.4 hp
Impeller speed: 126 rad/s
Impeller diameter: 61 cm
O_2 transfer: 3 lb/h/hp
O_2 correction factor: 0.83

Temperature: 25 °C
Windspeed: 4.47 m/s

Viscosity of air: 1.8×10^{-4} g/cm•s
Viscosity of water: 9×10^{-3} g/cm•s
Density of air: 1.2×10^{-3} g/cm^3
Diffusivity of O_2 in water: 2.4×10^{-5} cm^2/s
Density of liquid: 1 g/cm^3
Molecular weight of liquid: 18 g/g•mol
Molecular weight of air: 29 g/g•mol

Constituent: benzene with other biodegradable organics in water
Concentration (benzene): 10 g/m^3 (10 ppm)
Concentration (total organics): 250 g/m^3 (250 ppm)

Henry's law constant (benzene): 5.5×10^{-3} atm•m^3/g•mol
Diffusivity in air (benzene): 0.088 cm^2/s
Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s
Biorate (benzene and other organics): 5.28×10^{-6} g/s/g biomass
Biomass concentration: 4.0 g/L = 4,000 g/m^3

TABLE 4-9. INTERMEDIATE AND FINAL CALCULATION RESULTS FOR ACTIVATED SLUDGE MODEL UNIT

Quiescent zone:

$k_L = 6.5 \times 10^{-6}$ m/s

$k_g = 8.7 \times 10^{-3}$ m/s

$K = 6.5 \times 10^{-6}$ m/s

Turbulent zone:

$k_L = 1.3 \times 10^{-2}$ m/s

$k_g = 4.3 \times 10^{-2}$ m/s

$K = 5.5 \times 10^{-3}$ m/s

Overall mass transfer coefficient = 2.9×10^{-3} m/s

For well-mixed system:

$f_{air} = 0.83$

Emissions = 6.2×10^{-2} g/s = 2.0 Mg/yr

For plug-flow system:

$f_{air} = 0.90$

Emissions = 6.7×10^{-2} g/s = 2.1 Mg/yr

$$\frac{-d\,C_t\,(V)}{dt} = B\ b_i\ V\ C_t/C_o + KA\ C_t \qquad (4\text{-}29)$$

where

C_t = concentration in the impoundment as a function of time, g/m^3
t = time after disposal, s

and with the other symbols as previously defined. Rearranging Equation (4-29) gives:

$$\frac{d\,C_t}{C_t} = (-B\ b_i/C_o - KA/V)\ dt\ . \qquad (4\text{-}30)$$

Integrating Equation (4-30) from $C_t = C_o$ at $t = 0$ to $C_t = C_t$ at $t = t$ gives:

$$C_t/C_o = \exp\ (-B\ b_i t/C_o - KAt/V)\ . \qquad (4\text{-}31)$$

For an impoundment with a uniform depth, $V/A = D$. Substituting $V/A = D$ into Equation (4-31) yields:

$$C_t/C_o = \exp\ (-B\ b_i\ t/C_o - Kt/D)\ . \qquad (4\text{-}32)$$

When Equation (4-32) is evaluated after some fixed time t, the ratio C_t/C_o represents the fraction of the compound remaining in the impoundment; consequently, $1 - C_t/C_o$ represents the fraction that has been removed by biodegradation and air emissions. The fractions emitted to the air and biodegraded after some time (t) are calculated from their relative rates:

$$f_{air} = (1 - C_t/C_o)(KA)/(KA + B\ b_i\ V/C_o)\ . \qquad (4\text{-}33)$$

$$f_{bio} = (1 - C_t/C_o)(B\ b_i\ V/C_o)/(KA + B\ b_i\ V/C_o)\ . \qquad (4\text{-}34)$$

The quantity emitted after some time (t) is given by:

$$\text{Emitted quantity (g)} = f_{air}\ V\ C_o\ . \qquad (4\text{-}35)$$

The average emission rate over the period of time = t is:

$$E\ (g/s) = f_{air}\ V\ C_o/t\ . \qquad (4\text{-}36)$$

Alternatively, a simplifying assumption may be made that, because the impoundment is designed for disposal, all significantly volatile compounds are eventually emitted to the air. Emissions under this assumption would simply be QC_0 where Q equals the disposal rate in cubic meters/second. This assumption is probably valid for volatile compounds; however, compounds that are relatively nonvolatile may be removed slowly and the assumption may result in an overestimate of emissions.

4.5.2 Model Plant Parameters for Disposal Impoundments

The Westat data summary for impoundments indicated that disposal impoundments generally have higher surface areas and shallower depths than storage and treatment impoundments. The median surface area for disposal impoundments was approximately 9,000 m^2 (compared to 1,500 m^2 for storage impoundments), and the median depth was approximately 1.8 m. The disposal impoundment is assumed to be filled with waste every 6 mo (two turnovers per year).

The meteorological conditions and type of waste (water containing benzene and other organics for the example calculation are the same as those used for quiescent and aerated impoundments with biodegradation. The inputs for the example calculation of emissions from disposal impoundments are summarized in Table 4-10.

4.5.3 Example Calculations for Disposal Impoundments

Example calculations are presented below for the model unit defined to represent disposal impoundments.

a. Calculate liquid-phase mass transfer coefficient, k_L. Use Springer's model (see Table 4-1):

$$\text{Effective diameter} = \left(\frac{\text{Area}}{\pi}\right)^{0.5} \times 2 = \left(\frac{9{,}000}{\pi}\right)^{0.5} \times 2 = 107 \text{ m}$$

$$F/D = \text{Effective diameter/depth} = \frac{107}{1.8} = 59.5 \quad .$$

Windspeed = 4.47 m/s ($U_{10} \geq 3.25$ m/s)

F/D = 59.5

$$k_L = 2.611 \times 10^{-7}\ U_{10}^2 \left(\frac{D_w}{D_{ether}}\right)^{0.67} \text{ m/s}$$

TABLE 4-10. INPUT PARAMETERS--DISPOSAL IMPOUNDMENTS

Area: 9,000 m^2
Depth: 1.8 m
Volume: 16,200 m^3
Turnovers per year: 2

Temperature: 25 °C
Windspeed: 4.47 m/s

Diffusivity in water (ether): 8.5×10^{-6} cm^2/s
Viscosity of air: 1.81×10^{-4} g/cm•s
Density of air: 1.2×10^{-3} g/cm^3

Constituent: benzene with other biodegradable organics in water
Concentration (benzene): 10 g/m^3 (10 ppm)
Concentration (total organics): 250 g/m^3 (250 ppm)
Henry's law constant (benzene): 5.5×10^{-3} $atm \cdot m^3/g$ mol
Diffusivity in air (benzene): 0.088 cm^2/s
Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s
Biorate (benzene and other organics): 5.28×10^{-6} g/s/g biomass
Biomass concentration: 0.05 g/L = 50 g/m^3

where

U_{10} = windspeed = 4.47 m/s

$D_w = 9.8 \times 10^{-6}\ cm^2/s$ (benzene)

$D_{ether} = 8.5 \times 10^{-6} = cm^2/s$ (ether) .

Then

$$k_L = 2.611 \times 10^{-7}\ (4.47)^2 \left[\frac{9.8 \times 10^{-6}}{8.5 \times 10^{-6}}\right]^{0.67}$$

$k_L = 5.7 \times 10^{-6}$ m/s .

b. Calculate gas-phase mass transfer coefficient, k_g. Use MacKay and Matasugu (see Table 4-1):

$$k_G = 4.82 \times 10^{-3}\ U^{0.78}\ Sc_G^{-0.67}\ \ d_e^{-0.11} (m/s)$$

where

U = windspeed = 4.47 m/s

$$Sc_G = \text{Schmidt No. for gas} = \frac{\text{viscosity of gas}}{\text{(gas density)(diffusivity of i in gas)}}$$

Gas = air

Viscosity (air) = 1.81×10^{-4} g/cm•s

Density (air) = $1.2 \times 10^{-3}\ g/cm^3$

Diffusivity (benzene in air) = $0.088\ cm^2/s$

$$Sc_G = \frac{1.81 \times 10^{-4}\ g/cm{\bullet}s}{(1.2 \times 10^{-3}\ g/cm^3)\ (0.088\ cm^2/s)} = 1.71$$

d_e = effective diameter = 107 m .

Then

$$k_G = (4.82 \times 10^{-3})\ (4.47)^{0.78}\ (1.71)^{-0.67}\ (107)^{-0.11}$$

$$= 6.5 \times 10^{-3}\ m/s$$.

c. Calculate overall mass transfer coefficient, K:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keq\ k_G}$$

where

$$Keq = \frac{H}{RT} = \frac{5.5 \times 10^{-3}\ m^3 \bullet atm/mol}{(8.21 \times 10^{-5}) \left[\frac{atm \bullet m^3}{mol\ K}\right] (298\ K)} = 0.225 \quad .$$

Then

$$\frac{1}{K} = \frac{1}{5.7 \times 10^{-6}} + \frac{1}{(0.225)(6.5 \times 10^{-3})} = 1.76 \times 10^5$$

$$K = 5.7 \times 10^{-6}\ m/s \quad .$$

d. Calculate the biorate weighting factor and effective biorate for benzene in the mixture from Equation (4-28):

$B = 2.1 \times 10^{-7}$ g/s/g biomass (see Section 4.4.3, Step c) .

e. Calculate the fraction remaining from Equation (4-32). The impoundment is filled with waste initially, and 6 mo later it will be filled again. Calculate the fraction remaining after the initial 6-mo period:

$$C_t/C_o = \exp\ (-B\ b_i\ t/C_o - Kt/D)$$

$B = 2.1 \times 10^{-7}$ g/s/g biomass (effective biorate from Step d)

$b_i = 50\ g/m^3$

$t = 6\ mo = 1.58 \times 10^7\ s$

$C_o = 10\ g/m^3$

$K = 5.7 \times 10^{-6}\ m/s$

$D = 1.8\ m$

$$B\ b_i\ t/C_o = (2.1 \times 10^{-7}\ g/s/g\ biomass)(50\ g/m^3)(1.58 \times 10^7\ s)/10\ g/m^3 = 16.6$$

$$Kt/D = (5.7 \times 10^{-6}\ m/s)(1.58 \times 10^7\ s)\ /\ 1.8\ m = 50.0$$

$$C_t/C_o = \exp\ (-\ 16.6 - 50) = 0 \quad .$$

f. Calculate the fraction emitted from Equation (4-33):

$$f_{air} = (1 - C_t/C_o)(KA)\ /\ (KA + B\ b_i\ V/C_o)$$

$C_t/C_o = 0$

$KA = (5.7 \times 10^{-6}\ m/s)(9{,}000\ m^2) = 0.051/m^3/s$

$B\ b_i\ V/C_o = (2.1 \times 10^{-7}\ g/s/g\ biomass)(50\ g/m^3)(16{,}200\ m^3)/10\ g/m^3$

$= 0.017\ m^3/s$

$f_{air} = (1 - 0)(0.051\ m^3/s)\ /\ (0.051\ m^3/s + 0.017\ m^3/s)$

$f_{air} = 0.75$.

g. Calculate the average emission rate over the 6-mo period from Equation (4-36):

$E\ (g/s) = f_{air}\ V\ C_o/t$

$= (0.75)(16{,}200\ m^3)(10\ g/m^3)/1.58 \times 10^7\ s$

$= 7.7 \times 10^{-3}\ g/s.$

4.6 DIFFUSED AIR SYSTEMS

4.6.1 Emission Model Equations

Some impoundments and open tanks (e.g., activated sludge units) are sparged with air to promote biodegradation or air stripping. To estimate emissions from diffused air systems, the model assumes that the air bubbling through the liquid phase reaches equilibrium with the liquid-phase concentration of the constituent. The emissions leaving with the diffused air are estimated by:

$$E = Q_a K_{eq} C_L \qquad (4\text{-}37)$$

where

E = emissions, g/s

Q_a = air flow rate, m^3/s

K_{eq} = equilibrium constant

C_L = concentration in the liquid phase, g/m^3.

Emissions can also occur from wind blowing across the surface. If the air sparging creates a very turbulent surface similar to the surface of mechanically aerated systems, then the emission rate should be based on values of K typical for mechanically aerated systems. If the air sparging rate does not result in a turbulent surface, then K can be estimated from the correlations given for quiescent surfaces in Section 4.2.

The approach to estimate total emissions for flowthrough tanks and impoundments sparged with diffused air is similar to that described for quiescent and aerated systems. Because the unit is sparged with air, the liquid phase is assumed to be well mixed and the plug-flow model is not used. A material balance around this well-mixed system yields:

$$QC_o = KC_LA + Q_aKeqC_L + B\ b_i\ V\ C_L/C_o + QC_L \qquad (4\text{-}38)$$

where all of the symbols have been previously defined. The steady-state liquid phase concentration (C_L) is calculated by rearranging Equation (4-38):

$$C_L = \frac{QC_o}{KA + Q_aKeq + B\ b_i\ V/C_o + Q} \quad . \qquad (4\text{-}39)$$

Air emissions are estimated as the sum from wind blowing across the surface and from the diffused air:

$$E = KC_LA + Q_a\ Keq\ C_L \quad . \qquad (4\text{-}40)$$

For disposal impoundments with diffused air systems, the steady-state assumptions of the flowthrough models do not apply. Emissions are greatest when the waste is first placed in the impoundment and gradually decrease with time. To incorporate the contribution to mass transfer from diffused air, an equivalent mass transfer coefficient is defined:

$$K_D = KeqQ_a/A \qquad (4\text{-}41)$$

where

K_D = equivalent mass transfer coefficient for diffused air, m/s

and all of the other symbols are as previously defined.

The mass transfer coefficient for wind blowing across the surface (K) is calculated as described previously for flowthrough systems. An overall mass transfer coefficient (K') is defined as

$$K' = K_D + K \quad . \qquad (4\text{-}42)$$

The overall mass transfer coefficient (K') is used in the equations for disposal impoundments (Section 4.5.1) to estimate the fraction emitted

(Equation 4-33) and the average emission rate (Equation 4-36). The overall mass transfer coefficient defined above includes the mass transfer effects from both removal mechanisms (wind and diffused air).

4.6.2 Model Unit Parameters for Activated Sludge Unit with Diffused Air

A model unit for the activated sludge process was defined in Section 4.4.4 and Table 4-8. The same dimensions are used here to define an activated sludge unit that uses diffused air instead of mechanical aeration. The only additional parameter that must be specified is the diffused air rate, which typically ranges from 0.3 to 0.5 m^3/s per 1,000 m^3 of volume (20 to 30 ft^3/min per 1,000 ft^3 of volume).[55] For the model unit with a volume of 108 m^3, an estimate of 0.04 m^3/s is recommended based on the midpoint of the design range. The model unit input parameters are summarized in Table 4-11.

4.6.3 Example Calculation for Diffused Air Activated Sludge Unit

An example calculation is presented below for the model unit defined in Table 4-11.

a. Calculate the liquid-phase, gas-phase, and overall mass transfer coefficients. This procedure was illustrated for quiescent surfaces and the results for this model unit are given in Table 4-9:

$k_L = 6.5 \times 10^{-6}$ m/s

$k_g = 8.7 \times 10^{-3}$ m/s

$K = 6.5 \times 10^{-6}$ m/s.

b. Calculate the equilibrium constant, Keq. The compound is benzene in water, and Keq has been presented as 0.225 in the previous sample calculations (from Equation 4-4).

c. Calculate the equilibrium liquid concentration in the unit (C_L) from Equation (4-39):

$Q = 0.0075$ m^3/s

$C_o = 10$ g/m^3

$K = 6.5 \times 10^{-6}$ m/s

$A = 27$ m^2

$Qa = 0.04$ m^3/s

$Keq = 0.225$

TABLE 4-11. INPUT PARAMETERS--DIFFUSED AIR ACTIVATED SLUDGE UNIT

Area: 27 m^2
Depth: 4 m
Volume: 108 m^3
Retention time: 4 h
Flow: 0.0075 m^3/s
Quiescent area: 12.8 m^2
Diffused air rate: 0.04 m^3/s

Temperature: 25 °C
Windspeed: 4.47 m/s

Viscosity of air: 1.81×10^{-4} g/cm•s
Density of air: 1.2×10^{-3} g/cm^3
Diffusivity of O_2 in water: 2.4×10^{-5} cm^2/s
Density of liquid: 1 g/cm^3
Molecular weight of liquid: 18 g/g•mol
Molecular weight of air: 29 g/g•mol

Constituent: benzene with other biodegradable organics in water
Concentration (benzene): 10 g/m^3 (10 ppm)
Concentration (total organics): 250 g/m^3 (250 ppm)

Henry's law constant (benzene): 5.5×10^{-3} atm•m^3/g•mol
Diffusivity in air (benzene): 0.088 cm^2/s
Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s
Biorate (benzene and other organics): 5.28×10^{-6} g/s/g biomass
Biomass concentration: 4.0 g/L = 4,000 g/m^3

$B = 10/250 \times 5.28 \times 10^{-6} = 2.1 \times 10^{-7}$ g/s/g biomass (effective biorate, see Section 4.4.3, Step C)

$b_i = 4{,}000 \text{ g/m}^3$

$V = 108 \text{ m}^3$

$QC_o = (0.0075 \text{ m}^3\text{/s})(10 \text{ g/m}^3) = 0.075 \text{ g/s}$

$KA = (6.5 \times 10^{-6} \text{ m/s})(27 \text{ m}^2) = 1.76 \times 10^{-4} \text{ m}^3\text{/s}$

$QaKeq = (0.04 \text{ m}^3\text{/s})(0.225) = 9.0 \times 10^{-3} \text{ m}^3\text{/s}$

$Bb_iV/C_o = (2.1 \times 10^{-7} \text{ g/s/g biomass})(4{,}000 \text{ g/m}^3)(108 \text{ m}^3)/10 \text{ g/m}^3 = 9.1 \times 10^{-3} \text{ m}^3\text{/s}$

$C_L = 0.075 \text{ g/s}/(1.76 \times 10^{-4} + 9.0 \times 10^{-3} + 9.1 \times 10^{-3} + 7.5 \times 10^{-3}) \text{ m}^3\text{/s} = 2.9 \text{ g/m}^3$

d. Calculate air emissions from Equation (4-40).

$E = (6.5 \times 10^{-6} \text{ m/s})(2.9 \text{ g/m}^3)(27 \text{ m}^2) + (0.04 \text{ m}^3\text{/s})(0.225)(2.9 \text{ g/m}^3) = 2.7 \times 10^{-2} \text{ g/s} = 0.84 \text{ Mg/yr}.$

4.7 OIL FILM SURFACES

Some impoundments may have a floating film of oil on the surface. A rigorous approach to estimating emissions from this type of source would consider three resistances acting in series:

- From the aqueous phase to the oil
- Through the oil
- From the oil to the air.

Such an approach would require estimates of these three resistances and estimates of the equilibrium partitioning between both the aqueous and oil phases and the oil and air phases. Because these estimates are not generally available, a simplifying assumption is that the oil film is relatively thin and that mass transfer is controlled by the gas-phase resistance. For this case, Equation (4-2) reduces to:

$$K = k_G \, Keq \qquad (4\text{-}43)$$

where k_G is calculated from the correlation of MacKay and Matasugu (Table 4-1) and Keq is calculated from Raoult's law by:

$$Keq = P^* \rho_a \, MW_{oil}/(\rho_L MW_a P_o) \qquad (4\text{-}44)$$

where

Keq = dimensionless equilibrium constant

P^* = vapor pressure of the volatile compound of interest, atm

P_o = total pressure, 1 atm

ρ_a = density of air, g/cm^3

ρ_L = density of oil, g/cm^3

MW_{oil} = molecular weight of oil, g/g mol

MW_a = molecular weight of air, 28.8 g/g mol.

The value of K calculated above is substituted into the equations for flowthrough systems to estimate emissions. For the well-mixed flow models, C_o and C_L in Equations (4-1) and (4-6) represent the VO concentration in the oil phase (entering and leaving the impoundment, respectively), and the flowrate Q is the volumetric flowrate of oil. Biodegradation is neglected because the oil film inhibits the transfer of oxygen.

The procedure described above assumes that the oil layer in the impoundment is well mixed. For example, changes in wind direction in units with retention times on the order of days may tend to move the oil layer in different directions and result in mixing. However, some systems may be designed for or characterized by plug flow. This flow model assumes that the oil film moves across the impoundment's surface without backmixing. For plug flow of the oil film in flowthrough impoundments and tanks, the fraction of VO in the oil layer emitted to the air is given by Equation (4-11), and air emissions are estimated from Equation (4-12). In these equations, C_e is the VO concentration in the oily effluent, C_o is the initial concentration in the oil layer entering the impoundment, τ is the residence time, D is the oil-film thickness, and Q is the volumetric flowrate of oil.

For an oil film on a disposal impoundment, emissions are calculated as described in Section 4.5. However, biodegradation is neglected and Equation (4-32) reduces to:

$$C_t/C_o = \exp(-Kt/D) \qquad (4\text{-}45)$$

and the fraction emitted to the air is:

$$f_{air} = 1 - \exp(-Kt/D) \qquad (4\text{-}46)$$

where

C_t = concentration in the oil film at time = t

C_o = initial concentration in the oil film

D = oil-film thickness

and with the other symbols as previously defined. The average emission rate over the period of time equal to t is:

$$E\ (g/s) = f_{air}\ V\ C_o/t$$

where

V = volume of oil in the impoundment, m^3

and with the other symbols as previously defined. An example calculation of this approach is given in Section 5.0 for applying an oil film to soil, which is analogous to an oil film on a disposal impoundment because there is no flow out in either case and emissions are a function of the time since disposal.

4.8 DISCUSSION OF ASSUMPTIONS AND SENSITIVITY ANALYSIS

4.8.1 Removal Mechanisms

The organic constituents present in wastes that are treated, stored, or disposed of in surface impoundments and open tanks may leave the unit by any of several mechanisms. Because of the large open surface area and relatively high volatility of many organic constituents, emissions to the air may be a primary removal mechanism for certain constituents. Other constituents may be destroyed in impoundments and tanks specifically designed for biodegradation. Aeration is often used to supply oxygen to biologically active systems. Unfortunately, aeration also greatly enhances the mass transfer of organic constituents to the air. Other removal mechanisms include adsorption on solids, seepage through the ground, or degradation (e.g., by photolysis or hydrolysis). For flowthrough systems, the organic constituents may leave the unit with the effluent that will subsequently be treated, stored, or disposed of.

Initial studies suggest that emission to air is a primary removal mechanism, especially for volatile constituents. Biodegradation in specific systems, particularly for semivolatiles, may also be significant.

For flowthrough systems, the removal of semivolatiles with the effluent may also be a primary removal mechanism. Other forms of degradation, adsorption, and seepage are neglected in this analysis for several reasons. These mechanisms are not believed to be significant for most systems and most constituents; however, they may be removal routes in a specific system or for a specific constituent. For example, an open tank may be designed specifically for liquid-phase carbon adsorption. These mechanisms are also difficult to model in a manner that is generally applicable considering the relatively sparse data on such removal mechanisms, especially in hazardous waste impoundments and tanks. Consequently, the modeling effort focuses on mass transfer to the air and some consideration of biodegradation.

Numerous studies have been conducted to assess mass transfer to the air; these include theoretical assessments, correlations based on laboratory and bench-scale measurements, and field measurements at actual sources. Additional data on specific wastes have been collected in air-stripping studies as more air-stripping columns have been used to remove VO constituents from water. The result is that the state of knowledge of mass transfer from the liquid to the gas phase (e.g., ambient air) is probably advanced compared to the state of knowledge of other removal mechanisms. The level of confidence in the air emission models is probably highest for the volatile constituents because of very high mass transfer rates. The level of confidence is somewhat lower for the relatively nonvolatile constituents because of potentially significant rates of removal by other mechanisms.

Much of the data on the performance of systems designed for biodegradation are reported as total removal from measurement of the influent and effluent concentrations. This total would include removal to the air and biodegradation. Some studies have been conducted in closed systems in which the biodegradation rate may be measured directly (loss to the air is deliberately prevented). These data are useful for comparing the relative rates of removal by biodegradation among constituents and make possible a ranking of these constituents with respect to biodegradability. In addition, the estimated rate of biodegradation may be compared to the estimated rate of air emissions to assess the relative extent of each.

The biodegradation model has not been validated and is used in this report as an approximate measure of the extent of biodegradation. For any specific treatment system, measurements of actual biodegradation rates should be used if available. Any user of the biodegradation model should be aware that the predicted rate is very sensitive to the choice of values for the biorate, biomass concentration, and the concentration of organic constituents in the waste. An environmentally conservative approach with respect to air emissions would be to neglect biodegradation (assume the rate is zero). This approach is probably valid for volatile constituents in aerated systems; however, the approach may tend to overestimate emissions of relatively nonvolatile constituents that are destroyed in treatment systems specifically designed for biodegradation.

4.8.2 Major Assumptions

An inherent assumption in the emission estimating procedure is that the mass transfer correlations chosen earlier are generally applicable. A paper that compares several different models concludes that, in most cases, many different models yield comparable results for volatile constituents.[56] The choice of models may affect the estimated mass transfer coefficients for semivolatiles more than those for volatiles. The calculations indicate that emissions of volatiles are controlled by the liquid-phase resistance. Consequently, the value for the overall mass transfer coefficient (K) is primarily determined by the correlation used for the liquid-phase mass transfer coefficient (k_L). For constituents with decreasing volatility, both the liquid-phase and gas-phase resistance begin to contribute to the overall resistance to mass transfer. For these constituents, the choices of correlations for both k_G and k_L become important, and the choice of correlations may significantly affect the emission estimates.

The flow model chosen for storage and treatment impoundments assumes that the impoundment's contents are well mixed and that the system is operated at steady-state conditions. The flow for specific facilities may be better represented by plug flow or a model that accounts for axial dispersion. The choice of flow model does not make a significant difference in the estimated emissions. However, if the loading of the impoundment is cyclical or intermittent instead of continuous, the emissions from the impoundment are likely to be cyclical or intermittent. Estimates of short-term emission rates are very dependent upon the method of operation of the system. For disposal impoundments, peak emissions occur when the waste is first placed in the impoundment and then decrease with time. The approach used in this report estimates the average emission rate over a given period of time and does not provide an estimate of the initial peak emissions.

The calculation of Henry's law constant also contains inherent assumptions. The approach is valid for dilute solutions and has been applied successfully in the design of air-stripping columns. However, specific mixtures may deviate from Henry's law because of component interactions or because of concentrations outside the range of applicability. Errors in applying Henry's law are generally environmentally conservative; i.e., the actual gas-phase concentration is not likely to be underestimated.

For concentrated mixtures of organics in a separate oil layer, the use of Raoult's law is recommended. This approach is valid for mixtures of constituents with similar properties, especially when the concentration of the component of interest is very high. A preferred approach would be to avoid the use of Henry's law or Raoult's law and actually measure the equilibrium partitioning between the liquid and gas phase of a waste. However, very few data are available for equilibrium partitioning that can be applied generally to hazardous waste mixtures.

4.8.3 Sensitivity Analysis

The emission correlations were evaluated for sensitivity to each of the input parameters.[57] In the analysis, each input parameter was varied individually over the entire range of reasonable values. The effect on emissions was noted, and the most sensitive parameters were identified.

Detention time is an important parameter that affects emissions from the impoundment. The emission estimates for volatile constituents are sensitive to short detention times, and the estimates for semivolatiles are sensitive to long detention times. Essentially all of the volatile constituents are emitted for longer detention times (several days), and very little of the semivolatiles are emitted for short detention times (a few days). However, significant emissions of the semivolatiles may occur for long detention times in storage impoundments or in disposal impoundments.

The value of Henry's law constant was not important for volatile constituents. The correlations indicated that these constituents are controlled by the liquid-phase resistance, which is not affected by Henry's law constant. The value of Henry's law constant has a direct effect on the emissions of semivolatiles (such as phenol), and the greatest effect is on those relatively nonvolatile compounds for which mass transfer is controlled by the gas-phase resistance.

Windspeed has a direct effect on the emission estimates for quiescent surfaces and has little effect on those from aerated systems. The results showed that a standard windspeed of 4.5 m/s was reasonable compared with the results for windspeed distributions at actual sites.

Temperature did not affect the emission estimates for the volatile constituents. However, temperature did affect the emission estimates for nonvolatile constituents with mass transfer controlled by the gas phase. The temperature dependence of Henry's law constant accounts for this effect.

The diffusivity in air and water for a wide variety of constituents spans a relatively narrow range of values. The analysis showed that the emission estimates were not sensitive to the choice of values for diffusivity.

For mechanically aerated systems, the choice of values for impeller diameter, impeller speed, oxygen transfer rate, and oxygen correction factor did not affect the emission estimates significantly. The total horsepower and turbulent area had a direct effect on emissions of semivolatiles (e.g., phenol). However, there was no significant effect on emissions of volatile constituents because the models predicted that they would be stripped almost completely from the water over the full range of aeration values.

The biodegradation model was very sensitive to all parameters investigated. The sensitive parameters include organic concentration, biomass concentration, and biorate.

Two meteorological parameters required in the models are temperature and windspeed. The emission estimates are based on a standard temperature of 25 °C and a windspeed of 4.47 m/s (10 mi/h). These standard values were evaluated by estimating emissions for windspeed/temperature combinations at actual sites based on their frequency of occurrence. Over a 1-yr period, the results from site-specific data on windspeed and temperature were not significantly different from the results using the standard values. Consequently, the standard values were judged adequate to estimate annual emissions. For short-term emissions, the actual temperature and windspeed over the short-term interval should be used to avoid underestimating emissions during high-windspeed/high-temperature conditions.

A sensitivity analysis was performed for three impoundment model units (storage, mechanically aerated, and disposal) presented in the example calculations in this section. Three compounds were chosen to represent relatively nonvolatile compounds (p-cresol), moderately volatile compounds (acetone), and relatively volatile compounds (benzene). Each of these compounds can be biodegraded. The results are given in Tables 4-12, 4-13, and 4-14. The key input parameters identified in the tables were increased by 50 percent from the base case to determine the effect on the percent of the compound in the waste that is emitted to the air.

For each of the different types of impoundments, the volatility appears to be important only for the low volatility category. As discussed previously, the windspeed (air turbulence) has a direct effect for each of the compounds in a storage impoundment and does not affect the mechanically aerated unit's results. The low volatility compounds are the most sensitive to changes in depth and biomass concentration for all three types of impoundments. An assumption of no biodegradation also has the most dramatic effect on the low volatility compound with smaller effects observed for the higher volatility compounds. The effects of retention time are small except for the results shown for the disposal impoundment after 5 days. The disposal impoundment results show that for short times, the time since disposal is an important parameter affecting emissions.

TABLE 4-12. RESULTS OF SENSITIVITY ANALYSIS FOR QUIESCENT STORAGE IMPOUNDMENT

Key emission model inputs	Percent emitted for given Henry's law constant (atm•m^3/mole)		
	10^{-7}	10^{-5}	10^{-3}
Base case[a]	2.9	58	59
50-percent increase from base case[b]			
Volatility	4.2 (45)[c]	61 (5)	59 (0)
Air turbulence	4.0 (38)	72 (24)	76 (29)
Retention time	3.2 (10)	62 (7)	62 (5)
Depth	2.1 (-28)	50 (-14)	49 (-17)
Biomass concentration	2.1 (-28)	52 (-10)	52 (-12)
No biodegradation[d]	10 (245)	74 (28)	80 (36)

[a] This corresponds to the model unit for storage impoundments used in the example calculation.

[b] Each parameter is increased individually by 50 percent from its base case value.

[c] Values in parentheses are percent change from the base case.

[d] Base case with no biodegradation.

TABLE 4-13. RESULTS OF SENSITIVITY ANALYSIS FOR MECHANICALLY AERATED IMPOUNDMENTS

	Percent emitted for given Henry's law constant (atm•m^3/mole)		
Key emission model inputs	10^{-7}	10^{-5}	10^{-3}
Base case[a]	2.7	79	99
50-percent increase from base case[b]			
Volatility	3.9 (44)[c]	85 (8)	99 (0)
Air turbulence	2.8 (4)	80 (1)	99 (0)
Water turbulence	3.6 (33)	85 (8)	99 (0)
Retention time	2.7 (0)	80 (1)	99 (0)
Depth	1.8 (-33)	73 (-8)	98 (-1)
Biomass concentration	1.8 (-33)	73 (-8)	98 (-1)
No biodegradation[d]	20 (640)	94 (28)	100 (1)

[a] This corresponds to the model unit for mechanically aerated impoundments used in the example calculation.

[b] Each parameter is increased individually by 50 percent from its base case value.

[c] Values in parentheses are percent change from the base case.

[d] Base case with no biodegradation.

TABLE 4-14. RESULTS OF SENSITIVITY ANALYSIS FOR DISPOSAL IMPOUNDMENTS

	Percent emitted for given Henry's law constant (atm•m^3/mole)		
Key emission model inputs	10^{-7}	10^{-5}	10^{-3}
Base case[a]	13	93	92
50-percent increase from base case			
Volatility	18 (38)[b]	94 (1)	92 (0)
Air turbulence	17 (31)	96 (3)	96 (4)
Retention time[c]	2.3 (-82)	55 (-41)	72 (-22)
Depth	9 (-31)	89 (-4)	88 (-4)
Biomass	9 (-31)	89 (-4)	89 (-3)
No biodegradation[d]	84 (550)	100 (8)	100 (9)

[a] Based on the dimensions given in the example calculation, 100 mg/L of the constituent in 1,000 mg/L total organics, and a time since disposal of 12 months.

[b] Values in parentheses are percent change from base case.

[c] A retention time of 5 days was selected here to show the sensitivity to retention time soon after disposal.

[d] Base case with no biodegradation.

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5.0 LAND TREATMENT

This section presents the approach used to estimate air emissions from land treatment operations. Analytical models to estimate emissions, representative values of model input parameters, and example calculations are included.

5.1 NARRATIVE DESCRIPTION OF LAND TREATMENT AIR EMISSIONS

Land treatment is one of several land disposal methods used for final disposition of hazardous wastes. At land treatment facilities, wastes are either spread onto or injected into the soil, after which they are normally tilled into the soil. Other activities likely to occur at land treatment facilities include storage of wastes in tanks or surface impoundments, loading and unloading of wastes in vacuum trucks or dump trucks, and dewatering of wastes using filtration devices. All of these activities have emission points associated with them. The following paragraphs describe analytical models used to estimate emissions from the application, tilling, and final disposition of hazardous waste at a land treatment disposal site. Emissions from other land treatment activities, such as truck loading, storage tanks, and fugitive emissions from transfer and handling operations, are estimated using procedures described in Section 7.0 of this report.

Estimating emissions from land treatment may involve one to three independent steps depending on operating practices at a land treatment site. If waste is applied from a vacuum truck to the soil surface, allowed to remain on the surface for a period of time, and then tilled into the soil, emissions are estimated in three steps: (1) during application of waste onto the soil from a vacuum truck, (2) after waste application and before tilling, and (3) after tilling the waste into the soil. If waste is applied to the soil surface and immediately tilled into the soil, emissions are estimated in only two steps: (1) during waste application, and (2) after tilling. If waste is applied by subsurface injection and immediately tilled, only one step is required to estimate emissions.

This section presents three separate analytical models that can be used to estimate air emissions from separate land treatment activities. Primary emphasis is given to the RTI land treatment model that is used to calculate emissions from waste that is mixed with the soil. This condition may exist when waste has been applied to the soil surface and has seeped into the soil or when waste has been injected beneath the soil surface or has been tilled into the soil. The RTI land treatment model is described below in Subsection 5.2.1, which includes separate discussions of the following topics:

Subsection	Topic
5.2.1.2	Biodegradation
5.2.1.4	Effective diffusivity
5.2.1.5	Waste partitioning
5.2.1.10	Model selection rationale

If waste is applied to the soil and does not seep into the soil but remains on the soil surface as a visible oil film, emissions are estimated as the product of an overall mass transfer coefficient, constituent concentration, and surface area of the land treatment site. The model for calculating the mass transfer coefficient was developed by McKay and Matsuga and is briefly discussed in Subsection 5.2.3. Emissions from a waste stream as it is applied onto the soil surface from a vacuum truck, regardless of waste type, are also calculated as the product of an overall mass transfer coefficient, the surface area of the waste stream, and the concentration of a specific constituent. Preliminary calculations indicate that emissions from waste application are extremely small and can be ignored in most situations. Even so, a brief discussion of a model for estimating these emissions is presented in Subsection 5.2.2, and the model can be used if desired. Also included in this section are Subsection 5.2.4, which discusses representative values of input parameters for the analytical models, and Subsection 5.2.6, which presents example calculations using each of the three models presented.

At many existing land treatment sites, waste is applied onto the soil from a vacuum truck and is allowed to remain for about 24 hours before being tilled into the soil. Under these conditions, three separate calculations may be needed to estimate air emissions. Emissions during waste application could be estimated using the waste application model described in Subsection 5.2.2; emissions after application but before tilling would be estimated using the RTI land treatment model as described in Subsection 5.2.1 (or, if a visible oil film exists on the soil surface, the oil film surface model as presented in Subsection 5.2.3); and emissions after tilling would be estimated using the RTI land treatment model. At other existing sites, waste is injected into the soil using subsurface injection and is immediately tilled. At these sites, only one calculation is needed to estimate emissions. In this situation, the RTI land treatment model would be used.

5.2 LAND TREATMENT

5.2.1 Land Treatment Emission Model Descriptions

5.2.1.1 *Analytical Correlations*. Emissions from land treatment after waste is applied to the soil are estimated using a model developed by Clark Allen of Research Triangle Institute (the RTI model). This model assumes that emissions from the surface of the soil/waste mixture are limited by the diffusion of vapors through the pore spaces in the soil/waste mixture and further assumes that an equilibrium concentration of organic vapors exists at all times within the pore spaces. The model is based on Fick's second law of diffusion applied to a flat slab as described by Crank[1] and includes a term to estimate biological decay assuming a decay rate that is first order with respect to waste loading in the soil.

The solution to the diffusion equation developed by Crank is for diffusion out of a slab that initially has a uniform concentration of diffusing material throughout and that has equal concentrations of diffusing material at each surface.

The general solution to the diffusion equation for those conditions, as presented by Crank, is:

$$F = \frac{M_t}{M_o} = 1 - \sum_{n=o}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D\ (2n+1)^2 \pi^2 t}{4\ l^2}\right] , \qquad (5\text{-}1)$$

where

F = fraction of initially applied material that has diffused out of the slab at time t

M_t = mass of material that has diffused out of the slab at time t

M_o = initial mass of material present

D = diffusion coefficient

l = distance from center to surface of slab

t = time after initial distribution of diffusing material into the slab.

This series solution converges very slowly for small values of time (i.e., $Dt/l^2 < 0.213$). Because of this slow convergence at short times (i.e., immediately after waste application or tilling), Crank presented an alternative solution that is valid during this short time. The following equation is obtained from the alternative solution:

$$F = \frac{M_t}{M_o} = \frac{2}{\sqrt{\pi}} \left(\frac{Dt}{l^2}\right)^{1/2} \quad \left(\text{for } Dt/l^2 < 0.213\right) \quad . \tag{5-2}$$

Equation (5-2) approximates the Crank solution but excludes a small error function correction used by Crank.

To verify the validity of Crank's solution for short times and to test the accuracy of an approximation for use over longer times, the values predicted by the solution for short times and the values obtained using the first term of the series solution [Equation (5-3)] are compared to the values obtained using the first three terms of the series solution. Table 5-1 presents the results for a range of values of the dimensionless parameter, Dt/l^2:

$$F = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2 t}{4l^2}\right) \quad . \tag{5-3}$$

Table 5-1 shows that, for values of the dimensionless parameter greater than 0.213, the first term of the series solution, Equation (5-3),

TABLE 5-1. COMPARISON OF THE ESTIMATED FRACTION EMITTED USING THREE DIFFERENT EQUATIONS (INTEGRATED FLUX FROM SOIL)

Time parameter (Dt/l^2)	Short-term solution $2\left[\frac{Dt}{\pi l^2}\right]^{1/2}$	First term of series solution $1 - \frac{8}{\pi^2}\exp\left[-\frac{Dt\pi^2}{4l^2}\right]$	First three terms of series solution
0.000	0.000	0.189	0.067
0.025	0.178	0.238	0.179
0.050	0.252	0.284	0.252
0.075	0.309	0.326	0.309
0.100	0.357	0.367	0.357
0.125	0.399	0.405	0.399
0.150	0.437	0.440	0.437
0.175	0.472	0.474	0.472
0.200	0.505	0.505	0.504
0.213	0.521	0.521	0.520
0.250	0.564	0.562	0.562
0.275	0.592	0.589	0.589
0.300	0.618	0.613	0.613
0.325	0.643	0.636	0.636
0.350	0.668	0.658	0.658
0.375	0.691	0.679	0.679
0.400	0.714	0.698	0.698
0.425	0.736	0.716	0.716
0.450	0.757	0.733	0.733
0.475	0.778	0.749	0.749
0.500	0.798	0.764	0.764
0.525	0.818	0.778	0.778
0.550	0.837	0.791	0.791
0.575	0.856	0.804	0.803
0.600	0.874	0.816	0.816
0.625	0.892	0.827	0.827
0.650	0.910	0.837	0.837
0.675	0.927	0.847	0.847
0.700	0.944	0.856	0.856
0.725	0.961	0.864	0.865
0.750	0.977	0.873	0.873
0.775	0.993	0.880	0.880
0.800	1.009	0.887	0.887
0.825	1.025	0.894	0.894
0.850	1.040	0.900	0.900
0.875	1.056	0.906	0.906
0.900	1.070	0.912	0.912
0.925	1.085	0.917	0.917
0.950	1.100	0.922	0.922
0.975	1.114	0.927	0.927

can be used to estimate total emissions. The table also shows that the solution for short times, Equation (5-2), is valid for values of the dimensionless parameter below 0.213. Equations (5-2) and (5-3) give identical results for a parameter value of 0.213. This comparison indicates that sufficient accuracy can be attained under all conditions if the equation for short times is used for values of the dimensionless parameter below 0.213 and the first term of the general solution is used for values above 0.213. It is observed that the fraction of material that diffuses out of the slab is linear with respect to the square root of time up to the point where approximately 50 percent of the diffusing material is lost.[2]

The conditions defined for the above solutions by Crank are analogous to diffusion of volatile organics out of a surface layer of a soil/waste mixture as happens in land treatment operations. Because of the symmetry of conditions on which the above solutions are based, an impenetrable plane could, in theory, be inserted at the midpoint of the slab without changing the solution. One-half of the slab with an impenetrable boundary layer on the bottom would represent the surface layer of soil into which waste is mixed during land treatment.

In a land treatment operation, the applied material partitions into several phases including evaporation into a vapor phase, adsorption onto soil particles, and absorption into oil and water in the soil/waste mixture. Only the vapor phase is available for diffusion out of the soil/waste mixture. Therefore, to apply the above equations to land treatment, the amount of material in the vapor phase must be known. The amount of material that partitions into the vapor phase can be estimated by calculating equilibrium conditions within the soil/waste mixture. This equilibrium is estimated by defining Keq, the ratio of the amount of organics in the vapor phase to the total amount of organics in the soil/waste mixture. The instantaneous emission rate, E, at any time, t, can be estimated by the following Equations (5-4) and (5-5), which are obtained by differentiating Equations (5-2) and (5-3) and adding the equilibrium constant, Keq, and a term to account for waste biodegradation, $e^{(-t/t_b)}$:

(short times) $$E = \frac{M_o}{l}\left(\frac{K_{eq}D}{\pi t}\right)^{1/2} e^{-t/t_b} \quad , \qquad (5\text{-}4)$$

and

$$\text{(longer times)} \quad E = M_o \left[\frac{2KeqD}{l^2}\right] \exp\left[\frac{-KeqD\,\pi^2 t}{4l^2}\right] e^{-t/t_b} \quad . \qquad (5\text{-}5)$$

where

t_b = the biological degradation time constant.

The above equations account for the removal of organic material from the soil/waste mixture both biological degradation and air emissions. In a land treatment operation, the primary objective is to dispose of organic materials by biodegradation; thus, significant quantities of waste would be expected to be depleted from the soil by biological degradation. Other mechanisms of removal such as leaching and photolysis also are possible but are not accounted for in this model because of the estimated small amount of materials lost by these processes.

5.2.1.2 Biodegradation. Biodegradation at land treatment sites is generally considered to be a first-order process with respect to waste concentration in the soil up to the point where saturation is achieved.[3] In addition to literature sources that make such statements, comments on a draft of this document provided by Chevron Research Company offer further evidence of the first-order nature of biodegradation at land treatment sites.[4] A first-order decay process is defined in the literature as having the following form:[5]

$$\frac{dM}{dt} = -K_bM \quad ,$$

where

M = mass of organic material in the soil

K_b = biological decay constant.

Integrating and using the boundary conditions $M = M_o$ at $t = 0$ results in:

$$\frac{dM}{M} = -K_b dt \quad ,$$

$$\log M = -K_b t + C_1 \quad ,$$

or

$$M = C_2 e^{-K_b t} ,$$

where C_1 and C_2 are constants of integration. Substituting the boundary conditions gives:

$$M = M_o e^{-K_b t} .$$

K_b has units of s^{-1} and can be expressed as the reciprocal of the biological decay time constant, $1/t_b$. The exponential was introduced directly into the rate relationship, Equations (5-4) and (5-5), to reduce the amount of material available for air emissions by the fraction of material removed by biooxidation.

5.2.1.3 Estimation of Equilibrium Coefficient, Keq. Partitioning of volatile constituents in the waste is assumed to occur between the vapor space in the soil/waste mixture, adsorbent solids in the soil, and absorbent liquids in the soil and waste. Using 1 cm^3 of the soil/waste mixture as a basis for calculation, the total volume of gas (i.e., void space) in the cubic centimeter is described by the air porosity, ϵ_a. Using the ideal gas law, the number of moles of gas in 1 cm^3 of the soil/waste mixture is $P\epsilon_a/(RT)$, where P is the pressure of a constituent in the gas phase and is usually equal to XP^* (X is the mole fraction of the constituent in the liquid phase and P^* is the pure component vapor pressure). The moles of constituent in the gas phase in 1 cm^3 of the soil/waste mixture is thus $XP^*\epsilon_a/(RT)$. Oil loading in the soil/waste mixture in units of grams of oil per cubic centimeter of mixture is L (g_{oil}/cm^3 mixture), and the total moles of constituent per cubic centimeter of the mixture is XL/MW_{oil}. The equilibrium coefficient, Keq, is defined as the moles of constituent in the gas phase per unit volume of the soil/waste mixture divided by the total moles of constituent per unit volume of the soil/waste mixture. Therefore, the following equation can be written:

$$Keq = \frac{XP^*\epsilon_a/(RT)}{X\ L/MW_{oil}} = \frac{P^* MW_{oil} \epsilon_a}{RTL} .$$

This equation differs from the usual equation for equilibrium coefficient by the factor ϵ_a, which is included to account for the limited air space available within the soil/waste mixture. The ratio of moles per mole and grams per gram can be used interchangeably in this equation. The value of Keq can be calculated from measurements, if available, of constituent concentrations in the pore space and in the soil/waste mixture.

In a similar manner, it can be shown that Keq can be estimated for aqueous wastes with an assumed value of the Henry's law constant, H_c:

$$\mathrm{Keq} = \frac{H_c\, 10^6\, \epsilon_a}{RT\epsilon_{\mathrm{waste}}} .$$

where

$\epsilon_{\mathrm{waste}}$ = the volume fraction of the soil/waste mixture that is occupied by waste.

In the above equations, it is assumed that equilibrium is controlled by Raoult's law for oily wastes and by Henry's law for aqueous wastes.

5.2.1.4 Estimation of Effective Diffusivity. The diffusivity of specific compounds, as reported in the literature, assumes that the diffusion occurs in free air. In a land treatment operation, diffusion of vapors out of the soil must take place within the confines of the air-filled voids within the soil. This characteristic of soil is referred to as the air porosity. The ratio of effective diffusivity of a constituent in the soil to its diffusivity in air can be described by the following equation:[6]

$$\frac{D_e}{D_a} = \frac{\epsilon_a^{10/3}}{\epsilon_T^2} ,$$

where

D_e = effective diffusivity of constituent in soil

D_a = diffusivity of constituent in air

ϵ_a = air porosity of soil

ϵ_T = total porosity of soil.

When air porosity and total porosity are the same (i.e., for dry soil), this equation reduces to:

$$\frac{D_e}{D_a} = \epsilon_a^{4/3} \quad .$$

Total porosity refers to the fraction of the land treatment medium that is made up of nonsoil (or nonsolid) materials, i.e., the sum of the void space, water-filled space, and space occupied by the oil in the applied waste.

Soil air porosity undergoes substantial changes over time as soil dries out and when moisture is added by rainfall or by watering. As a result, accurately accounting for soil porosity in an analytical model is difficult. The use of average or typical values of soil porosity may be the most practical approach.

5.2.1.5 Waste Partitioning. A large percentage of wastes that are disposed of by land treatment are refinery sludges. These wastes are mostly sludge emulsions and consist of varying fractions of water, oil, and inorganic solids, where oil represents the total organic portion of the waste including volatile compounds. A much smaller amount of land-treated wastes are dilute aqueous solutions of water and organic compounds. When wastes are applied to a land treatment area, volatile materials in the soil have the potential for partitioning into four different phases--a vapor phase, an oil phase where volatile material is dissolved in the oil, a water phase where volatile material is absorbed in the soil moisture, and a soil phase where volatile material is adsorbed by organic carbon within the soil. For oily wastes, VO compounds will preferentially dissolve in oil rather than water so that the fraction of volatile materials in the water phase is estimated to be very small. Partitioning of volatile materials into the soil phase by adsorption is a function of the amount of organic carbon in the soil but is also estimated to account for only a small fraction of the applied organics because of the high loading rates normally used in land treatment. An equilibrium equation can be written that takes all four phases into account in the estimation of equilibrium vapor concentration in the soil. However, as presented here, the equilibrium equation in the RTI model includes only two phases. Calculations by one researcher looked at the difference in estimated emissions using two-phase partitioning of waste into an oil phase and vapor phase and using four-phase partitioning. The results of these comparisons are given in Table 5-2 and show for the conditions considered that, for soils having an organic carbon content of up to 10 percent, the estimated fraction of applied organics emitted using four-phase partitioning is only about 10 percent less than the estimated fraction emitted using two-phase partitioning. In a given situation, the amount of material adsorbed by organic carbon in the soil is relatively constant; thus, in soils with high organic carbon content, adsorption of materials in the soil may become more significant if low loading rates are used. One of the products of biodegradation is organic carbon; thus, land treatment sites that have been active for an extended time may have elevated concentrations of organic carbon. Even so, with the normal oil loading used in land treatment, it is likely that a large fraction of the available adsorption sites would be occupied by the oil itself, thus limiting the effects of adsorption on emissions of the lighter constituents.

For oily sludges, Keq is calculated using vapor pressure and waste loading is calculated exclusive of water content. For dilute aqueous waste, partitioning is estimated to be in a water phase and a vapor phase, and the parameter Keq is calculated using Henry's law constant; waste loading is calculated using the total waste applied. Keq may be calculated from site-specific land treatment soil, vapor, and solids analyses if available. Table 5-3 summarizes the equations that make up the RTI land treatment model.

5.2.1.6 Emissions at Short Times. When a sludge containing volatile organics is applied onto or tilled into the soil at a land treatment site, the maximum rate of air emissions will occur immediately after application or tilling. Volatile organics will leave the surface and enter the environment through wind currents. Although the RTI model is based on the premise that emissions from land treatment are limited by vapor diffusion through the soil, the maximum rate of air emissions immediately after application or tilling will be limited by the gas-phase mass transfer

TABLE 5-2. EMISSION ESTIMATES USING TWO DIFFERENT EQUATIONS FOR THE VAPOR-SOIL PARTITION COEFFICIENT[7]

Organic carbon content of soil (fraction)	Estimated emission fraction--two-phase partitioning	Estimated emission fraction--four-phase partitioning
0	0.622	0.622
0.001	0.622	0.621
0.010	0.622	0.614
0.100	0.622	0.559

TABLE 5-3. RTI MODEL FOR LAND TREATMENT EMISSIONS

Emission rate equations

Short-term solution ($Keq\ D_e t/l^2 < 0.213$)

$$E = \frac{M_o}{l}\left[\frac{1}{\frac{\epsilon_a}{Keq\ k_G} + \left(\frac{\pi t}{D_e\ Keq}\right)^{1/2}}\right] e^{-t/t_b}$$

Long-term solution ($Keq\ D_e t/l^2 \geq 0.213$)

$$E = M_o\left[\frac{2Keq\ D_e}{l^2}\right] \exp\left(-\frac{Keq\ D_e\ \pi^2\ t}{4l^2} - \frac{t}{t_b}\right)$$

Fraction air emissions

Short-term solution [$t/t_b < 0.5$ and ($Keq\ D_e t/l^2) < 0.25$]

$$F_{at} = \left(\frac{KeqD_e t}{\pi l^2}\right)^{1/2} 2\left(1 - 1/3\ t/t_b\right)$$

Long-term solution ($K_d t_b \geq 0.22$)

$$F_{at} = \frac{8}{\pi^2}\left(1 + \frac{1}{K_d t_b}\right)^{-1}\left[1 - \exp\left(-K_d t - t/t_b\right)\right] + 0.1878$$

Long-term solution ($K_d t_b < 0.22$)

$$F_{at} = F_a\ [1 - \exp\ (-K_d t - t/t_b)]$$

Very long-term solution ($t \to \infty$) ($K_d t_b \geq 0.62$)

$$F_a = \frac{0.811\ K_d\ t_b}{(K_d\ t_b + 1)} + 0.1878$$

Very long-term solution ($t \to \infty$) ($K_d t_b < 0.62$)

$$F_a = \left(\frac{Keq\ D_e t_b}{l^2}\right)^{1/2}$$

(continued)

TABLE 5-3 (continued)

$$Keq = \frac{P^{*}MW_{oil}}{RT} \frac{\epsilon_a}{L}$$ (used for oily sludges)[a]

$$Keq = \frac{H_c}{RT} (10^6) \frac{\epsilon_a}{\epsilon_{waste}}$$ (used for dilute aqueous waste)[a]

$$k_G = 4.82\ (10^{-3})\ U^{0.78}\ Sc_G^{-0.67}\ de^{-0.11}$$

$$Sc_G = \frac{\mu a}{\rho_a D_a}$$

$$M_o = LlC$$

$$K_v = \frac{KeqD_e}{l^2}$$ (volatilization constant)

$$K_d = \frac{\pi^2}{4} K_v$$

$$D_e = D_a \left[\frac{\epsilon_a^{10/3}}{\epsilon_T^{2}}\right]$$ (if both air porosity and total porosity are known)

$$de = \left(\frac{4A}{\pi}\right)^{0.5}$$

$$D_e = D_a\ \epsilon_a^{4/3}$$ (if only air porosity is known)

$$t_b = \frac{4.83\ (10^7)}{B}$$

$L = \frac{W f_{oil}}{Al}$ (for oily sludges); $L = \frac{W}{Al}$ (for dilute aqueous waste)

Variable	Definition	Data source
Keq	Equilibrium coefficient of constituent in the soil (dimensionless)	Calculated

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[a] Equilibrium equations are adjusted to account for volume fractions of air and waste within the soil.

(continued)

TABLE 5-3 (continued)

Variable	Definition	Data source
k_G	Gas-phase mass transfer coefficient (cm/sec)	Calculated
C	Concentration (weight fraction) of constituent in the oil phase or (for dilute aqueous waste) in water	Definition
D_a	Diffusion coefficient of constituent in air, cm^2/s	Data base
D_e	Effective diffusion coefficient of constituent in the soil, cm^2/s	Calculated
E	Emission rate of constituent, $g/cm^2/s$	Calculated
H_c	Henry's law constant for constituent, $atm \bullet cm^3/g$ mol	Data base
l	Depth to which waste is mixed in the soil, cm	Literature
L	Oil or aqueous waste loading in the soil, g/cm^3	Calculated from annual throughput
M_t	Air emissions of constituent from the soil, g/cm^2	Calculated
M_o	Initial loading of constituent on the land treatment site, g/cm^2	Calculated
MW_{oil}	Average molecular weight of the oil, g/g mol	Estimated
MW	Molecular weight of constituent, g/g mol	Data base
p^*	Pure component vapor pressure of constituent, atm	Data base
R	Ideal gas constant, 82.1 $atm \bullet cm^3/g$ $mol \bullet K$	Literature
t	Time after waste application to the land treatment site, s	Definition
t_b	Time constant for biological decay of constituent, s[b]	Literature

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[b] Time constant is the time required for biodegradation of 63.2 percent of a pollutant.

(continued)

TABLE 5-3 (continued)

Variable	Definition	Data source
T	Temperature of vapor in soil, K	Assumed
ϵ_a	Volume fraction of air-filled voids in the soil (soil air-filled porosity) (dimensionless)	Estimated from literature data
ϵ_T	Total porosity of the soil (equivalent to dry basis bulk density divided by soil particle density) (dimensionless)	Estimated
ϵ_{waste}	Volume fraction of waste in the soil (dimensionless)	Calculated
B	Biorate of constituent, mg VO/g•h	Data base
K_v	Volatilization constant for constituent, s^{-1}	Calculated
K_d	Modified volatilization constant, s^{-1}	Calculated
K_b	Biodegradation constant for constituent, s^{-1}	Calculated
F_a	Fraction of constituent emitted to the air after a long time	Calculated
F_{at}	Fraction of constituent emitted to the air at time t	Calculated
f_{oil}	Fraction by weight of applied waste that is oil (organic)	Definition
U	Windspeed, m/s	Estimated
W	Total waste applied to land treatment site, g	Definition
A	Area of land treatment site to which waste is applied, cm^2 (m^2 in calculation of de)	Definition
Sc_G	Schmidt number (gas phase)	Calculated
de	Effective diameter of land treatment area, m	Calculated
μa	Viscosity of air, g/cm•s	Literature
ρa	Density of air, g/cm^3	Literature

coefficient, k_G. Within a few hours after application or tilling, the rate of air emissions from the volatile components will be substantially less than the maximum rate because the volatiles at the surface have been removed by the wind and the remaining volatiles must diffuse up through a layer of porous solids, a relatively slow process.

The equation for the emission rate immediately after application or tilling is:

$$E = \frac{M_o}{l} \left[\frac{1}{\dfrac{\epsilon_a}{k_G\ Keq} + \sqrt{\dfrac{\pi t}{D_e\ Keq}}}\right] e^{-t/t_b} \quad . \tag{5-6}$$

The basis of the above equation is a resistance in series model where the resistance (inverse of the mass transfer coefficient) is the sum of the resistance of the soil and the resistance at the wind-porous solid interface. The mass transfer coefficient of the soil is defined in Equation (5-4) in the term $\left(\frac{Keq\ D}{\pi t}\right)^{1/2}$. The resistance of the soil to mass transfer is the inverse of the above or $\left(\frac{Keq\ D}{\pi t}\right)^{-1/2}$. The resistance at the air-soil interface is defined by $\frac{1}{Keq\ k_G}$. Because Keq has previously been defined as containing a factor to account for soil porosity, this factor (soil porosity) must be included in the above equation to maintain a consistent definition of Keq throughout this discussion. The revised resistance is represented by $\frac{\epsilon_a}{Keq\ k_G}$. Summing the two resistances and substituting into Equation (5-4) gives Equation (5-6). The gas-phase mass transfer coefficient, k_G, is calculated as described in Table 4-1 for a surface impoundment.

5.2.1.7 Estimating the Fraction Emitted at Short Times. The fraction of a constituent emitted to the air after some time, t, can be estimated by integrating the equation for air emissions from time 0 to time t:

$$F_{at} = \left(\frac{Keq\ D_e}{\pi\ l^2}\right)^{1/2} \int_o^t t^{-1/2}\ e^{-t/t_b}\ dt \quad .$$

The exponential term can be replaced by a series,

$$e^{-t/t_b} = 1 - \frac{t}{t_b} + \frac{1}{2}\left(\frac{t}{t_b}\right)^2 - \frac{1}{6}\left(\frac{t}{t_b}\right)^3 - \frac{1}{24}\left(\frac{t}{t_b}\right)^4 - \ldots ,$$

which can be substituted into the above integral, and each of the individual terms integrated. The results of these integrations are:

$$F_{at} = \left[\frac{Keq\ D_e}{\pi\ l^2}\right]^{1/2} 2t^{1/2} \left[1 - \frac{1}{3}\left(\frac{t}{t_b}\right) + \frac{1}{10}\left(\frac{t}{t_b}\right)^2 - \frac{1}{42}\left(\frac{t}{t_b}\right)^3 + \ldots\right] .$$

This series solution converges with only a few terms for values of t/t_b less than 1. Therefore, the following simplification can be used to estimate the fraction emitted (i.e., integrated emissions) at short times:

$$F_{at} = \left[\frac{Keq\ D_e}{\pi\ l^2}\right]^{1/2} 2t^{1/2} \left[1 - \frac{1}{3}\frac{t}{t_b}\right] . \qquad (5\text{-}7)$$

The resistance to emissions presented by gas-phase mass transfer at the soil surface is only considered important for the estimation of the emission rates immediately after application or tilling. This resistance is omitted in the above equation with little loss in accuracy.

The above equation is used to predict the fraction of a constituent emitted to the air when the ratio t/t_b is less than 0.5 and when $KeqD_et/l^2$ is less than 0.25.

5.2.1.8 Estimating the Fraction Emitted for Longer Times. For longer times, when most of the constituent is not present in the soil, the short-term solution (Equations (5-4) and (5-7)) will overestimate air emissions. Under these conditions, Equation (5-5) can be integrated to estimate the fraction removed by volatilization. Equation (5-5) can be simplified by defining the constant, K_d, as $\dfrac{Keq\ D_e\ \pi 2}{4\ l^2}$:

$$E = \frac{M_o 8K_d}{\pi^2} \exp\left[-K_d t - t/t_b\right] . \qquad (5\text{-}8)$$

Integrating from time 0 to t gives:

$$F_{at} = \frac{8}{\pi^2}\left[1 + \frac{1}{K_d t_b}\right]^{-1}\left[1 - \exp\left[-K_d t - t/t_b\right]\right] + 0.1878 \quad . \qquad (5\text{-}9)$$

In the above equation, terms after the first ($n > 0$) in the series solution are replaced by the constant 0.1878. This equation is used for estimating air emissions when $K_d t_b$ is greater than or equal to 0.22.

When $K_d t_b$ is less than 0.22, the following simplification can be used to estimate air emissions at longer times. An exponential decay factor is established to relate the fraction emitted at any time, t, to the fraction emitted at very long times (i.e., $t \rightarrow \infty$) as estimated using Equation (5-12), which follows. The resulting equation is:

$$F_{at} = F_a\left[1 - \exp\left(-K_d t - t/t_b\right)\right] \quad . \qquad (5\text{-}10)$$

where

F_a = fraction of constituent emitted at very long times ($t \rightarrow \infty$).

For very long times (i.e., $t \rightarrow \infty$), the fraction emitted can be estimated using the following procedure. The integrated form of the general solution without dropping terms is:

$$F_{at} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1 - \exp\{-(2n+1)^2 K_d t - t/t_b\}}{(2n+1)^2 + \frac{1}{t_b K_d}} \quad .$$

This equation can be simplified using the following rationale: For large values of t, the exponential terms are negligibly small, and for large values of n, $1/(t_b K_d)$ becomes negligibly small compared to $(2n+1)^2$. If these conditions are true for all terms where $n > 0$, the simplified equation is:

$$F_a = \frac{8}{\pi^2}\left[\frac{K_d t_b}{K_d t_b + 1} + 0.2317\right] \quad .$$

The value of 0.2317 was obtained by evaluating the first 125 terms of the series for $n > 0$ with negligibly small values of $1/(t_b K_d)$:

$$\sum_{n=1}^{125} \frac{1}{(2n+1)^2} = 0.2317 \quad .$$

Combining terms and simplifying, the equation becomes:

$$F_a = \frac{0.81057K_dt_b}{K_dt_b + 1} + 0.1878 \quad . \qquad (5\text{-}11)$$

The assumptions used in developing Equation (5-11) are not valid for small values of K_dt_b ($K_dt_b < 0.62$). The solution under these conditions is approximated by the following relationship:

$$F_a = \sqrt{\frac{Keq\ D_e}{l^2}\ t_b} \quad . \qquad (5\text{-}12)$$

This relationship was established by using multiple terms of the general solution to calculate values of F_a for a series of input values for the parameters $KeqD_e/l^2$, which is identified as the volatilization constant, K_v, and t_b and then using a curve-fitting routine to derive the relationship in Equation (5-12) for $K_dt_b < 0.62$.

Table 5-4 presents the results of calculations of the long-term fraction emitted (i.e., $t \rightarrow \infty$) using 100 terms of the general solution and inputting several values of the dimensionless ratio, K_vt_b, designated as T. This ratio is an indicator of the relative rates of volatilization and degradation. Table 5-4 also shows the results if the above approximating equations are used to calculate the long-term fraction emitted, and it shows good agreement between these results and the results obtained by the general solution.

Table 5-5 shows a comparison of the estimated emission fractions for a range of values of K_vt and t/t_b using the first 100 terms of the general solution and using the approximations given in Equations (5-7) and (5-9). This table shows good agreement between the approximating equations and the rigorous solution.

To calculate the amount of waste remaining in the soil at any time, it is necessary to know both the amount emitted to the air and the amount

TABLE 5-4. ESTIMATED AIR EMISSION FRACTION AT LONG TIMES

Value of T $\left[T = K_v t_b\right]$	Estimated fraction (rigorous equation)	Estimated fraction[a]	Estimated fraction[b]
0.050	0.222	0.224	0.277
0.100	0.313	0.316	0.348
0.150	0.381	0.387	0.407
0.200	0.435	0.447	0.456
0.250	0.480	0.500	0.497
0.300	0.518	0.548	0.533
0.350	0.551	0.592	0.563
0.400	0.579	0.632	0.590
0.450	0.604	0.671	0.614
0.500	0.626	0.707	0.635
0.550	0.646	0.742	0.654
0.600	0.664	0.775	0.672
0.650	0.680	0.806	0.687
0.700	0.694	0.837	0.701
0.750	0.708	0.866	0.714
0.800	0.720	0.894	0.725
0.850	0.731	0.922	0.737
0.900	0.741	0.949	0.747
0.950	0.751	0.975	0.750
1.000	0.760	1.000	0.765
1.050	0.768	1.025	0.773
1.100	0.776	1.049	0.780
1.150	0.783	1.072	0.787
1.200	0.789	1.095	0.794
1.250	0.796	1.118	0.800
1.300	0.802	1.140	0.805
1.350	0.807	1.162	0.811
1.400	0.813	1.183	0.816
1.450	0.818	1.204	0.821
1.500	0.822	1.225	0.826
1.550	0.827	1.245	0.830
1.600	0.831	1.265	0.834
1.650	0.835	1.285	0.839
1.700	0.839	1.304	0.842
1.750	0.843	1.323	0.846
1.800	0.846	1.342	0.849
1.850	0.850	1.360	0.853
1.900	0.853	1.378	0.856
1.950	0.856	1.396	0.859
2.000	0.859	1.414	0.862

[a] $F_a = T^{0.5}$.

[b] $F_a = \dfrac{0.81057\ K_d t_b}{K_d t_b + 1} + 0.1878$.

TABLE 5-5. RIGOROUS VS. APPROXIMATE ESTIMATES OF EMISSION FRACTIONS

t/t_b	$K_v t$	$K_v t_b$	Estimated fraction (rigorous)	Estimated fraction (approximated by)[a]	Estimated fraction (approximated by)[b]
0.01	0.05	5.00	0.25	0.25	0.28
0.01	0.10	10.00	0.35	0.36	0.36
0.01	0.15	15.00	0.43	0.44	0.44
0.01	0.20	20.00	0.50	0.50	0.50
0.01	0.25	25.00	0.56	0.56	0.56
0.01	0.30	30.00	0.61	0.62	0.61
0.01	0.35	35.00	0.65	0.67	0.65
0.01	0.40	40.00	0.69	0.71	0.69
0.01	0.45	45.00	0.73	0.75	0.73
0.01	0.50	50.00	0.76	0.79	0.76
0.01	0.55	55.00	0.79		0.79
0.01	0.60	60.00	0.81		0.81
0.01	0.65	65.00	0.83		0.83
0.01	0.70	70.00	0.85		0.85
0.01	0.75	75.00	0.87		0.87
0.01	0.80	80.00	0.88		0.88
0.01	0.85	85.00	0.90		0.90
0.01	0.90	90.00	0.91		0.91
0.01	0.95	95.00	0.92		0.92
0.01	1.00	100.00	0.93		0.93
0.10	0.05	0.50	0.24	0.24	0.28
0.10	0.10	1.00	0.34	0.34	0.36
0.10	0.15	1.50	0.42	0.42	0.43
0.10	0.20	2.00	0.49	0.49	0.49
0.10	0.25	2.50	0.54	0.55	0.54
0.10	0.30	3.00	0.59	0.60	0.59
0.10	0.35	3.50	0.64	0.65	0.64
0.10	0.40	4.00	0.67	0.69	0.68
0.10	0.45	4.50	0.71	0.73	0.71
0.10	0.50	5.00	0.74	0.77	0.74
0.10	0.55	5.50	0.77		0.77
0.10	0.60	6.00	0.79		0.79
0.10	0.65	6.50	0.81		0.81
0.10	0.70	7.00	0.83		0.83
0.10	0.75	7.50	0.85		0.85
0.10	0.80	8.00	0.86		0.86
0.10	0.85	8.50	0.87		0.88
0.10	0.90	9.00	0.89		0.89
0.10	0.95	9.50	0.90		0.90
0.10	1.00	10.00	0.91		0.91
0.30	0.05	0.17	0.23	0.23	0.27
0.30	0.10	0.33	0.32	0.32	0.34
0.30	0.15	0.50	0.39	0.39	0.41
0.30	0.20	0.67	0.46	0.45	0.46
0.30	0.25	0.83	0.51	0.51	0.52

See notes at end of table.

(continued)

TABLE 5-5 (continued)

t/t_b	K_vt	K_vt_b	Estimated fraction (rigorous)	Estimated fraction (approximated by)[a]	Estimated fraction (approximated by)[b]
0.30	0.30	1.00	0.56	0.56	0.56
0.30	0.35	1.17	0.60	0.60	0.60
0.30	0.40	1.33	0.63	0.64	0.64
0.30	0.45	1.50	0.67	0.68	0.67
0.30	0.50	1.67	0.70	0.72	0.70
0.30	0.55	1.83	0.72		0.73
0.30	0.60	2.00	0.75		0.75
0.30	0.65	2.17	0.77		0.77
0.30	0.70	2.33	0.79		0.79
0.30	0.75	2.50	0.80		0.80
0.30	0.80	2.67	0.82		0.82
0.30	0.85	2.83	0.83		0.83
0.30	0.90	3.00	0.84		0.84
0.30	0.95	3.17	0.85		0.86
0.30	1.00	3.33	0.86		0.87
1.00	0.05	0.05	0.19	0.17	0.25
1.00	0.10	0.10	0.26	0.24	0.30
1.00	0.15	0.15	0.32	0.29	0.35
1.00	0.20	0.20	0.37	0.34	0.40
1.00	0.25	0.25	0.42	0.38	0.44
1.00	0.30	0.30	0.46	0.41	0.47
1.00	0.35	0.35	0.49	0.44	0.51
1.00	0.40	0.40	0.52	0.48	0.54
1.00	0.45	0.45	0.55	0.50	0.56
1.00	0.50	0.50	0.58	0.53	0.59
1.00	0.55	0.55	0.60		0.61
1.00	0.60	0.60	0.62		0.63
1.00	0.65	0.65	0.64		0.65
1.00	0.70	0.70	0.66		0.67
1.00	0.75	0.75	0.68		0.68
1.00	0.80	0.80	0.69		0.70
1.00	0.85	0.85	0.71		0.71
1.00	0.90	0.90	0.72		0.72
1.00	0.95	0.95	0.73		0.74
1.00	1.00	1.00	0.74		0.75

[a] Approximated by: $F_{at} = 1.128 \sqrt{K_v t}\ (1-1/3\ t/t_b)$.

[b] Approximated by: $F_{at} = \frac{8}{\pi^2} \left[1 + \frac{1}{K_d t_b}\right]^{-1} \left[1 - \exp\left(-K_d t - t/t_b\right)\right] + 0.1878$.

biodegraded. At very long times (i.e., t → ∞), all waste is assumed to disappear from the soil. Thus, the fraction of waste emitted plus the fraction biodegraded must be equal to 1 if other mechanisms of removal are ignored. Therefore, at very long times:

$$F_b = 1 - F_a \quad , \tag{5-13}$$

where

F_b = fraction of constituent that is biodegraded after a long time (i.e., t → ∞).

5.2.1.9 Tilling. To apply the model to a situation where the land treatment plot is retilled after the initial waste application and tilling, estimates of the amount of waste emitted to the air and the amount biodegraded are required. When retilling occurs, the amount of material remaining in the soil at the time of retilling is estimated using the following equation:

$$F_S = (1 - F'_{at})\, e^{-t/t_b} \quad , \tag{5-14}$$

where

F_S = fraction of constituent remaining in the soil

F'_{at} = fraction of material emitted to the air at time t assuming no biodegradation (F'_{at} can be estimated by setting $t/t_b = 0$ in Equation (5-7) or (5-9), whichever is appropriate).

To continue modeling emissions after retilling occurs, M_o is set equal to $F_S M_o$ and t is reset to zero. If a reapplication of waste occurs, the total waste loading is the sum of the waste remaining in the soil and the newly applied waste:

$$M_o = F_S M_o + M_n \quad , \tag{5-15}$$

where

M_n = amount of constituent newly applied to the land treatment site.

To continue the modeling after waste reapplication and tilling, t is reset to zero.

5.2.1.10 Model Selection. The RTI model was selected for use in this regulatory effort after a review of three models of land treatment emissions. The models reviewed were the RTI model, the Thibodeaux-Hwang model, and a model developed by EPA's Office of Research and Development located in Ada, Oklahoma (the Ada model). The review considered three selection criteria: technical basis, representativeness, and availability of inputs.

The Ada model is the most ambitious of the three in attempting to account for mechanisms of pollutant removal other than air emissions and biodegradation. However, that model requires detailed site-specific model inputs that may not be available or reasonably estimated. Because of these characteristics of the Ada model, it was not considered appropriate for use in the current effort. Both the Thibodeaux-Hwang and the RTI models have input requirements that are reasonably available, both have been compared with available measured data, and both have shown reasonable agreement with the measurements.[8] Apparently, either of these two models is satisfactory as a means of estimating emission rates at specific times for some organic compounds. However, if the Thibodeaux-Hwang model is used to estimate long-term, steady-state emissions, it would predict that all of the applied volatile organics are emitted because it does not account for biodegradation. Such a prediction would contradict data obtained from laboratory and field studies that indicate biodegradation of some organic compounds in land treatment applications.[9] The RTI model, in contrast, estimates biodegradation of individual compounds based on constituent-specific biodegradation rates. The RTI and the Thibodeaux Hwang models predict similar emission rates for initial volatile losses in the absence of biodegradation. Thus, the results of the RTI model show varying levels of biodegradation when used to evaluate the fate of different organic compounds.

In summary, the Ada model has had limited public review, accounts for multiple waste removal mechanisms, requires numerous detailed model inputs, and has no published comparisons of estimated and measured emissions. The Thibodeaux-Hwang model has been publicly reviewed, accounts for one major waste removal mechanism (volatilization), requires reasonably available model inputs, and there are published comparisons of measured and estimated emissions. The RTI model has had limited public review, accounts for the two major waste removal mechanisms (volatilization and biodegradation), requires reasonably available model inputs, and there are published comparisons of measured and estimated emissions. The peer review, emission comparisons, and data availability are compelling reasons for using the Thibodeaux-Hwang model. However, the absence of biodegradation in that model is considered a major shortcoming because of the importance attached to this removal mechanism by industry personnel and many independent researchers. Emission comparisons and data availability for the RTI model are roughly equivalent to those of the Thibodeaux-Hwang model, and the RTI model includes terms that account for biodegradation. The RTI and the Thibodeaux models predict similar emission rates for initial volatile losses in the absence of biodegradation. Thus, the RTI model was selected for use in the standards development process even though it has not been subjected to the extensive peer review that has been given to the Thibodeaux-Hwang model.

5.2.2 Waste Application Model

At land treatment facilities that do not use subsurface injection with immediate tilling, emissions may occur during the time that waste is being applied to the soil surface and while the waste lies on the soil before it is tilled into the soil. No existing models were identified that predict emissions during application of an oily sludge to the soil surface. The approach selected for this case was to calculate an overall mass transfer coefficient of volatile material from the surface of the stream of sludge as it falls from the end of a hose to the soil surface. The mass transfer coefficients were calculated using an equation presented in Section 4.0 (Table 4-1). The constant in the equation for gas-phase resistance was increased by a factor of two in an attempt to account for an increase in mass transfer caused by the motion of the waste stream through the air. The equations for making this calculation are presented in Table 5-6 along with the definitions of the variables used and the sources of input data.

5.2.3 Oil Film Model

Emissions from waste lying on the soil surface are estimated in either of two ways depending on the form of the waste as it lays on the soil

TABLE 5-6. WASTE APPLICATION EMISSION MODEL

Emission equations

$$E = KCA$$

$$A = 2\pi rl$$

$$K = Keq\ k_G \text{ (used for oily sludges); } \frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keqk_G} \text{ (used for dilute aqueous waste);}$$

$$k_G = 9.64(10^{-3})U^{0.78}Sc_G^{-0.67}de^{-0.11};$$

$$Keq = \frac{H}{RT} \text{ (used for dilute aqueous waste)}$$

$$Keq = \frac{P^*}{P_o}\frac{\rho_a\ MW_{oil}}{\rho_L\ MW_{air}} \text{ (used for oily sludges)}$$

$$k_L = 1\ (10^{-6}) + 144\ (10^{-4})\ U^{*2.2}\ Sc_L^{-0.5};\ Sc_L = \frac{\mu_L}{\rho_w D_w}$$

$$de = \left(\frac{4A}{\pi}\right)^{0.5};\ Sc_G = \frac{\mu_a}{\rho_a Da}$$

$$U^* = 0.01U(6.1 + 0.63U)^{0.5}$$

Variable	Definition	Data source
E	Emission rate for constituent, g/s	Calculated
K	Overall mass transfer coefficient, m/s	Calculated
Keq	Equilibrium coefficient, dimensionless	Calculated
H	Henry's law constant for constituent, atm cm^3/g mol	Literature
R	Universal gas constant, atm cm^3/g mol K	Literature
T	Temperature, K	Measured
P^*	Vapor pressure of constituent, mm Hg	Literature
P_o	System pressure (atmospheric pressure), mm Hg	Definition

(continued)

TABLE 5-6 (continued)

Variable	Definition	Data source
k_G	Gas-phase mass transfer coefficient, m/s	Calculated
U	Windspeed, m/s	Definition
Sc_G	Schmidt number on gas side	Calculated
Sc_L	Schmidt number on liquid side	Calculated
μ_a	Viscosity of air, g/cm•s	Literature
ρ_w	Density of water, g/cm^3	Literature
ρ_a	Density of air, g/cm^3	Literature
ρ_L	Density of oil, g/cm^3	Estimated
D_a	Diffusivity of constituent in air, cm^2/s	Literature
A	Surface area of cylindrical waste stream, m^2	Calculated
r	Radius of cylindrical waste stream, m	Measured
l	Length of cylindrical waste stream, m	Measured
C	Concentration of constituent in the waste, g/cm^3	Measured
de	Effective diameter of waste stream surface area, m	Calculated
MW_a	Molecular weight of air, g/g mol	Literature
MW_{oil}	Molecular weight of oil, g/g mol	Estimated
μ_L	Viscosity of water, g/cm•s	Literature
D_w	Diffusivity of component in water, cm^2/s	Data base
U^*	Friction velocity, m/s	Calculated
k_L	Liquid-phase mass transfer coefficient, m/s	Calculated

surface. If the applied waste has a visible oil film on top, emissions are estimated by calculating an overall mass transfer coefficient as described in Section 4.0 for an oil film on a surface impoundment. The mass transfer equation was developed by McKay and Matsuga and is based on data obtained from liquid hydrocarbon spills on land and water.[10] The equations used to calculate emissions under this situation are given in Table 5-7 along with definitions of the variables used. In situations where the applied waste does not have a visible oil film on top, the RTI land treatment model can be used to estimate emissions. The equation for short-term emissions given above as Equations (5-4) and (5-7) would be used for this situation.

5.2.4 Model Inputs

Typical values of input parameters for the RTI model are based primarily on a data base developed by EPA[11] from site visits and contacts with State, regional, and industry sources supplemented by information from recent literature. These values were chosen as reasonably representative of average or typical practices currently used at land treatment operations. Oil loading in the soil is a model input that is calculated from several other parameters that might change independently. Varying the value of the oil loading rate, thus, has the same effect as varying any one or any combination of the other parameters. Oil loading is defined by waste throughput, the percent oil in the waste, area of the land treatment site, and the depth to which the waste is mixed in the soil (tilling depth). Typical values of oil loading are defined from median values for those parameters by which it is defined. The data base shows annual throughput varying from about 2 Mg/yr to about 400,000 Mg/yr with a median value of about 1,800 Mg/yr. The area of land treatment sites ranges from less than 1 hectare (ha) to about 250 ha with a median value of 5 ha. The data base shows tilling depth varying from 15 cm to one case of 65 cm, with most being in the range of 15 to 30 cm. The single most frequently reported tilling depth is 20 cm, which is selected as a typical value. This value is in line with values of 15 to 30 cm reported in another study.[12] The data base shows oil content of the waste streams varying from about 2 to 50 percent, with a median value of about 12 percent and a mode value of 10 percent. The 10-percent figure is selected as typical.

TABLE 5-7. OIL FILM SURFACE EMISSION MODEL

Emission rate equation

$$E = KC_tA$$

$$C_t = C_o\ [\exp\ (-Kt/D)]$$

$$K = k_G\ Keq \text{ (used for oily sludges)}$$

$$k_G = 4.82\ \ (10^{-3})\ \ U^{0.78} Sc_G{}^{-0.67} de^{-0.11}$$

$$Sc_G = \frac{\mu_a}{\rho_a D_a}$$

$$Keq = \frac{P^*}{P_o}\ \frac{\rho_a MW_{oil}}{\rho_L MW_{air}} \text{ (used for oily sludges);}$$

$$de = \left(\frac{4A}{\pi}\right)^{0.5}$$

Variable	Definition	Data source
E	Emission rate for constituent, g/s	Calculated
K	Overall mass transfer coefficient, m/s	Calculated
C_t	Concentration of constituent in the oil phase at time t	Calculated
C_o	Initial concentration of constituent in the waste	Definition
D	Oil film thickness, m	Measured
A	Area of land treatment, m^2	Measured
k_G	Gas-phase mass transfer coefficient, m/s	Calculated

(continued)

TABLE 5-7 (continued)

Variable	Definition	Data source
U	Windspeed, m/s	Definition
Sc_G	Schmidt number--gas phase	Calculated
μ_a	Viscosity of air, g/cm•s	Literature
ρ_a	Density of air, g/cm^3	Literature
D_a	Diffusion coefficient of constituent in air, cm^2/s	Literature
de	Effective diameter of land treatment area, m	Calculated
Keq	Equilibrium coefficient of constituent	Calculated
P^*	Vapor pressure of constituent, mm Hg	Literature
P_o	Atmospheric pressure, mm Hg	Definition
MW_{oil}	Molecular weight of the oil, g/g mol	Definition
MW_a	Molecular weight of air, g/g mol	Literature
ρ_L	Density of oil, g/cm^3	Estimated
R	Universal gas constant, atm cm^3/g mol K	Literature
T	Temperature, K	Measured

Average molecular weight of the oil from which a particular constituent evaporates is one of the determining factors in the rate of evaporation and thus must be specified. Little data are available as guidance for selecting a value for this parameter. The distribution of constituents by molecular weight in land-treated wastes is not well known. In one field measurement study of land treatment emissions,[13] a value of 282 g/g mol was used as the average molecular weight of the oil. This value was based on distillation of oil from a refinery sludge and identification of the constituent corresponding to the midpoint distillation temperature (i.e., the temperature at which 50 percent of the oil was distilled). The value 282 g/g mol is selected for use. A sensitivity analysis using the RTI model shows that emissions are not highly sensitive to this parameter.

Soil air porosity and total porosity impact the effective diffusivity of a constituent in the soil. Very little soil porosity information has been identified. One study reported measured values of soil porosity in a land treatment plot as ranging from 43.3 to 65.1 percent,[14] with an average value of about 50 percent. The literature values are assumed to represent air porosity. Total soil porosity would include the air porosity and the space occupied by oil and water within the soil. One field study reported measured values of both total porosity and air-filled porosity.[15] Measured values of total porosity ranged from 54.7 to 64.8 percent, with an average value of 60.7 percent. Measured values of air-filled porosity ranged from 27.4 to 46.9 percent, with an average of 37.2 percent. The value of 61 percent for total porosity is assumed to be a representative value. A value of 0.5 is used in the model as a default for air porosity.

Biorate data used in the RTI model data base (CHEMDAT6) represent measured rates in aqueous systems. In order to use the aqueous biorate data in a land treatment process, a factor was established for converting aqueous data to land treatment values using measured data for benzene. A recent publication by the American Petroleum Institute (API) reported experimentally determined values of biological decay constants for land treatment studies using two different soil types.[16] Decay constants were measured for six compounds including two compounds, benzene and toluene, that have aqueous biorates in the land treatment model data base (CHEMDAT6). For benzene, the ratio of the API data, measured in units of day^{-1}, and the aqueous data, measured in units of mg VO/$g_{biomass}$•hr, was calculated as 0.00179. This value is also a close approximation of the ratio of the two data points for toluene, the other compound for which data from both sources were available. The other compounds for which data were reported by API did not have referenced aqueous data in the data base. The above calculated relationship was used to calculate equivalent aqueous data values for those compounds. Reported and calculated values of aqueous biorates and land treatment biological decay constants are presented in Table 5-8. The ratio of 0.00179 is used for all compounds to convert from aqueous biorates to decay constants that can be used in the land treatment model. The input parameter for the land treatment model is a biological decay time constant, t_b, in units of seconds. The equation for calculating t_b from the aqueous biorate is derived as follows.

The biological decay time constant is, by definition, equal to the reciprocol of the biological decay constant, or

$$t_b = \frac{1}{K_b} , \tag{5-16}$$

where K_b = biological decay constant. The ratio, r, of decay constant to aqueous biorate is:

$$r = \frac{K_b}{B} \frac{g_{bio} \ h}{mg \ VO \ day} \text{ or } K_b = rB \ day^{-1} .$$

Substituting into Equation (5-16) gives:

$$t_b = \frac{1}{rB} \ day .$$

To obtain a result in seconds, this equation must be multiplied by 86,400 s/day. Making this conversion and inserting the value of r (i.e., 0.00179) gives:

$$t_b = \frac{86,400}{0.00179 \ B} = \frac{4.83 \ (10^7)}{B} .$$

For situations in which petroleum wastes are landfarmed and no information is known about the nature of the volatile materials, it is

TABLE 5-8. MEASURED AND ESTIMATED BIORATES AND DECAY CONSTANTS FOR SELECTED ORGANIC CONSTITUENTS

Organic constituent	Aqueous biorate, mg $VO/g_{biomass}\cdot h$	Calculated decay constant, day^{-1}	Measured decay constant, day^{-1}[a]	
			Nunn[b]	Kidman[c]
Benzene	19.0	0.034	0.034	0.013
Ethylbenzene	46.4[d]	0.083	0.083	0.076
Xylene(-o)	40.8[d]	0.073	0.073	0.026
Naphthalene	42.5[d]	0.076	0.076	0.050
Toluene	73.5	0.132	0.106	0.119
Methyl naphthalene	24.0[d]	0.043	0.043	0.059

[a] Reference 17.

[b] Data obtained using a clay loam soil (Nunn soil).

[c] Data obtained using a sandy loam soil (Kidman soil).

[d] Values calculated from API experimental data.

possible to estimate a default biorate from the average decay constant values reported in the API investigation, 0.07 day^{-1}, which corresponds to a biorate, B, of 40 mg/g-h. This value is between the values for benzene and toluene in the data base. The average value of the biological rate constant in the two soils investigated by API was not significantly different.

In summary, parameters and selected typical values for use in the RTI model are as follows:

Annual waste throughput = 1,800 Mg

Area of land treatment = 5 ha

Oil content of waste = 10 percent

Average molecular weight of the oil = 282 g/g mol

Soil air porosity = 0.5

Soil total porosity = 0.61

Tilling depth = 20 cm

Temperature = 25 °C.

5.2.5 Estimation of Total VO Emissions

The preceding discussion has been limited to estimating emissions of a single constituent in a hazardous waste. Using the models presented here to estimate total VO emissions can be accomplished using any of several approaches. The most obvious approach, and the one that should give the most accurate results, would be to obtain a detailed analysis of the constituents in the waste being land treated. The emission equations could be used to calculate emissions of each constituent, and total emissions could be calculated by summing the emissions of individual constituents. In many cases, a detailed analysis of the applied waste may not be available, and other, less accurate methods may be needed to estimate total VO emissions. An alternative to the constituent approach could make use of a boiling curve or steam stripping test of a sample of the waste. Experimental data developed by Chevron Research Company[18] indicate that a large fraction of the constituents that boil at temperatures of 400 °F or lower will be emitted to the atmosphere and that those constituents with higher boiling points will tend to remain in the soil for a sufficient time to undergo biodegradation. Similar results are obtained by applying the RTI land treatment model to the constituents in the CHEMDAT6 data base. If a sample of waste were subjected to a laboratory boiling test or other equivalent test at a temperature of 400 °F, the fraction of oil evaporated would approximate the fraction that potentially would be emitted to the air in a land treatment operation.

A third approach to estimating total VO emissions would again make use of the experimental results generated by Chevron Research. The test results showed that approximately 25 percent of the applied oil in the land treatment test was emitted to the air. In the absence of a detailed constituent analysis and with no boiling or steam stripping test of the waste, a crude estimate of total VO emissions could be made by assuming that emissions are equal to 25 percent of the applied oil. This approximating alternative would only apply to raw oily refinery wastes that have not undergone any pretreatment to remove VO.

5.2.6 Example Calculations

5.2.6.1 Emissions from Land Treatment Soil. The following calculation demonstrates the use of the RTI model to calculate the long-term fraction of applied material emitted to the atmosphere and to calculate the short-term and long-term emission rates and emission fractions. The calculations are made for benzene at a concentration of 2,000 ppm by weight in a waste stream that is 10 percent oil.

Input values are:

Land area = 2.5 ha (half of total area of 5 ha assumed active)
Annual throughput = 1,800 Mg
Oil content of waste = 10% (by weight)
Benzene concentration in oil = 2,000 ppm (by weight) (2 mg/g oil)
Tilling depth = 20 cm
Soil air porosity = 0.5
Soil total porosity = 0.61
Average molecular weight of oil = 282 g/g mol .

a. Calculate oil loading (Equation from Table 5-3):

$$L = \frac{(1{,}800 \times 10^6\ g_{waste})(0.1\ g_{oil}/g_{waste})}{(2.5 \times 10^8\ cm^2)(20\ cm)} = 0.036\ g_{oil}/cm^3\ .$$

b. Identify constituent properties:

Benzene properties:

$B = 19.00$ mg $VO/g_{biomass} \cdot h$

$D_a = 0.088\ cm^2/s$

$P^* = 95.2$ mm Hg $= 0.125$ atm.

c. Calculate the equilibrium coefficient (Equation from Table 5-3):

$$Keq = \frac{P^*\ MW_{oil}\ \epsilon_a}{RT\ L} = \frac{(0.125\ atm)(282\ g/g\ mol)(0.5\ cm^3/cm^3)}{(82.05\ atm \cdot cm^3/g\ mol \cdot K)(298\ K)(0.036\ g/cm^3)}$$

$$Keq = 0.02002\ .$$

d. Calculate the biological degradation time constant (Equation from Table 5-3):

$$t_b = \frac{4.83(10^7)}{B} = \frac{4.83\ (10^7)}{19} = 2.54\ (10^6)\ s\ .$$

e. Calculate the effective diffusivity of constituent in the soil (Equation from Table 5-3):

$$D_e = D_a \frac{\epsilon_a^{10/3}}{\epsilon_T^{2}} = 0.088\ cm^2/s\ \frac{(0.5)^{10/3}}{0.61^2} = 0.0235\ cm^2/s\ .$$

f. Calculate the value of $K_d = \dfrac{\pi^2 KeqD_e}{4\ l^2}$:

$$K_d = \frac{(9.87)\ (0.0235)\ cm^2/s\ (0.02002)}{4\ (400)\ cm^2} = 2.9\ (10^{-6})\ s^{-1}\ .$$

g. Calculate the fraction of constituent emitted to the air after a long time (Equation (5-11)):

$$F_a = \frac{0.81\ K_d t_b}{K_d t_b + 1} + 0.1878 = 0.90 \quad .$$

h. Calculate the long-term emission rate after 60 h (216,000 s).

$$\text{Keq}\ \frac{D_e t}{l^2} = \frac{0.02002 \times 0.0235 \times 216{,}000}{400} = 0.254 \quad .$$

Use Equation (5-5) (long-term equation):

$$E = M_o\ \frac{2\text{Keq}\ D_e}{l^2}\ e \left[\frac{-\text{Keq}\ D_e\ \pi^2 t}{4\ l^2}\right]\ e^{-t/t_b}$$

$$E = \frac{2 \times 0.72 \times 2 \times 0.02002 \times 0.0235}{400} \times e \left[\frac{-0.02002 \times 0.0235 \times 9.87 \times 216{,}000}{1{,}600}\right]$$

$$\times\ e[-216{,}000/2.54(10^6)]$$

$$= 3.38(10^{-6})\ e(-0.627)\ e(-0.085) = 3.38(10^{-6})\ e(-0.712)$$

$$E = 3.38(10^{-6})\ (0.491) = 1.7(10^{-6})\ \frac{\text{mg}}{\text{cm}^2\ \text{s}} \quad .$$

c. Calculate the short-term emission rate after 15 min (900 s):

$$\text{Keq}\ \frac{D_e t}{l^2} = \frac{0.02002 \times 0.0235\ (900)}{400} = 0.0010$$

$$k_G = 4.82\ (10^{-3})\ U^{0.78}\ Sc_G^{-0.67}\ de^{-0.11} \quad ,$$

where

U = windspeed = 4.47 m/s

de = effective diameter of land treatment area

$$de = \left(\frac{4A}{\pi}\right)^{0.5} = 178\ \text{m}$$

$$Sc_G = \frac{\mu g}{\rho_a\ D_a}$$

where

μg = viscosity of air = 1.81(10^{-4}) g/cm•s

ρ_a = density of air = 1.2 (10^{-3}) g/cm^3

D_a = 0.088 cm^2/s

$$Sc_G = \frac{1.81\ (10^{-4})}{1.2\ (10^{-3})(0.088)} = 1.71$$

$$k_G = 4.82(10^{-3})\ (4.47)^{0.78}\ (1.71)^{-0.67}\ (178)^{-0.11} = 0.0061 \text{ m/s} = 0.61 \text{ cm/s}$$

$$E = \frac{M_o}{l}\left[\frac{1}{\dfrac{\epsilon_a}{k_G\ Keq} + \sqrt{\dfrac{\pi t}{De\ Keq}}}\right] e^{-t/t_b}$$

$$E = \frac{0.72 \text{ g } 2 \text{ mg}}{1 \text{ cm}^2\ 20 \text{ cm g}}\left[\frac{1}{\dfrac{0.5}{0.61 \times 0.02002} + \sqrt{\dfrac{3.14 \times 900}{0.0235 \times 0.02002}}}\right] e(-900/2.54(10^6))$$

$$= 0.072\ (0.0004)\ e(-0.0004) = 2.87\ (10^{-5})\ \frac{\text{mg}}{\text{cm}^2\ \text{s}}\ .$$

Table 5-9 shows estimated emission rates and emission fractions for various times up to 40 days (960 hours).

5.2.6.2 Emissions from Waste Application. The following is an example calculation for the application of an oily waste to a land treatment plot using the equations in Table 5-6. For benzene in waste oil, the calculation is:

Input values:

r = 0.038 m

L = 0.46 m

μ_a = 1.81 (10^{-4}) g/cm•s

ρ_a = 1.2 (10^{-3}) g/cm^3

U = 4.47 m/s

R = 82.05 atm•cm^3/K•g mol

T = 298 K

TABLE 5-9. ESTIMATED EMISSION RATES AND FRACTIONS EMITTED VERSUS TIME FOR EXAMPLE LAND TREATMENT CALCULATION

Time after application/tilling, h	Emission rate, 10^{-6} mg/cm^2•s	Equation used	Fraction emitted, fraction	Equation used
1	14.4	Short term	0.073	Short term
2	10.3	Short term	0.104	Short term
4	7.30	Short term	0.147	Short term
8	5.12	Short term	0.207	Short term
24	2.90	Short term	0.356	Short term
48	1.98	Short term	0.497	Short term
96	1.08	Long term	0.674	Long term
192	0.348	Long term	0.827	Long term
480	0.011	Long term	0.899	Long term
960	0.00004	Long term	0.901	Long term

C = 200 ppm = 200 μg/g = 0.0002 g/cm^3 = 200 g/m^3
(assuming a density of 1 g/cm^3)

$A = 2\pi rL = 2(3.14)(0.038 \text{ m})(0.457 \text{ m}) = 0.11 \text{ m}^2$

$\rho_L = 1 \text{ g/cm}^3$

$MW_a = 29 \text{ g/g mol}$

$MW_{oil} = 282 \text{ g/g mol.}$

a. Calculate the effective diameter of the waste stream surface (Equation from Table 5-6):

$$de = \left(\frac{4A}{\pi}\right)^{0.5} = 0.37 \text{ m} \quad .$$

b. Calculate the Schmidt number (Equation from Table 5-6):

$$Sc_G = \frac{\mu_a}{\rho_a \, D_a} = \frac{1.81\ (10^{-4}) \text{ g/cm}\cdot\text{s}}{[1.2\ (10^{-3}) \text{ g/cm}^3](0.088 \text{ cm}^2\text{/s})} = 1.71 \quad .$$

c. Calculate the equilibrium coefficient (Equation from Table 5-6):

$$Keq = \frac{P^*}{P_o} \frac{\rho_a \, MW_{oil}}{\rho_L \, MW_a} = \frac{(95.2 \text{ mm Hg})[1.2\ (10^{-3}) \text{ g/cm}^3](282 \text{ g/g mol})}{(760 \text{ mm Hg})(1 \text{ g/cm}^3)(29 \text{ g/g mol})} = 0.0015 \quad .$$

d. Calculate the gas-phase mass transfer coefficient (Equation from Table 5-6):

$$k_G = 9.64(10^{-3})\ U^{0.78}\ Sc_G^{\ -0.67}\ de^{-0.11}$$

$$= 9.64(10^{-3})(4.47)^{0.78}(1.71)^{-0.67}(0.37)^{-0.11}$$

$$= 0.024 \text{ m/s} \quad .$$

e. Calculate the overall mass transfer coefficient (Equation from Table 5-6):

$$K = k_G\ Keq = (0.0015)(0.024) \text{ m/s} = 0.000036 \text{ m/s} \quad .$$

f. Calculate emissions from a unit volume of waste (Equation from Table 5-6):

$$E = KCA = 0.000036 \text{ m/s} \ (200 \text{ g/m}^3) \ (0.11) \text{ m}^2$$

$$= 7.92 \ (10^{-4}) \text{ g/s} \ .$$

Using a calculated fall time of 0.305 s:

$$E = (7.92 \cdot 10^{-4} \text{ g/s})(0.30 \text{ s}) = 2.38 \ (10^{-4}) \text{ g} \ .$$

$$\text{Stream volume} = \pi r^2 L = (3.14)(0.038 \text{ m})^2 (0.46 \text{ m}) = 0.002 \text{ m}^3$$

$$= 2{,}073 \text{ cm}^3 \ .$$

$$\text{Mass of constituent} = (0.002 \text{ m}^3) \ (200 \text{ g/m}^3) = 0.4 \text{ g} \ .$$

g. Calculate the fraction of constituent emitted to the air:

$$\text{Fraction emitted} = \frac{2.38(10^{-4})\text{g}}{0.4 \text{ g}} = 0.00059 = 0.06\% \ .$$

5.2.6.3 Emissions from an Oil Layer on Soil Prior to Tilling. An example calculation for butanol-1 in an oil layer on the soil surface of a land treatment site is given below using the equation from Table 5-7.

Input values:

μ_a = $1.81 \ (10^{-4})$ g/cm•s
ρ_a = $1.2 \ (10^{-3})$ g/cm^3
U = 4.47 m/s
MW_{oil} = 282 g/g mol
ρ_L = 1 g/cm^3
MW_a = 29 g/g mol
C = 0.0002 g/cm^3 = 200 g/m^3
A = 25,000 m^2
t = 24 h = 86,400 s
d = 0.072 m .

a. Calculate the effective diameter of the soil surface (Equation from Table 5-7):

$$de = \left(\frac{4 \ A}{\pi}\right)^{0.5} = \left(\frac{4 \times 25{,}000}{\pi}\right)^{0.5} = 178 \text{ m} \ .$$

b. Calculate the Schmidt number (Equation from Table 5-7):

$$Sc_G = \frac{\mu_a}{\rho_a D_a} = \frac{1.81\ (10^{-4})\ \text{g/cm}\bullet\text{s}}{[1.2\ (10^{-3})\ \text{g/cm}^3](0.080\ \text{cm}^2/\text{s})} = 1.885\quad .$$

c. Calculate the equilibrium coefficient (Equation from Table 5-7):

$$Keq = \frac{P^*\ \rho_g\ MW_{oil}}{P_o\ \rho_L\ MW_a} = \frac{(6.5\ \text{mm Hg})[1.2\ (10^{-3})\ \text{g/cm}^3](282\ \text{g/g mol})}{(760\ \text{mm Hg})\ (1\ \text{g/cm}^3)\ (29\ \text{g/g mol})}$$

$$= 1.0\ (10^{-4})\quad .$$

d. Calculate the gas-phase mass transfer coefficient (Equation from Table 5-7):

$$k_G = 4.82\ (10^{-3})\ U^{0.78}\ Sc_G^{-0.67}\ de^{-0.11} = 4.82(10^{-3})(4.47)^{0.78}(1.89)^{-0.67}(178)^{-0.11}$$

$$= 5.7\ (10^{-3})\quad .$$

e. Calculate the overall mass transfer coefficient (Equation from Table 5-7):

$$K = k_G\ Keq = [5.7\ (10^{-3})\ \text{m/s}][1.0\ (10^{-4})] = 5.70\ (10^{-7})\ \text{m/s}\quad .$$

f. Calculate the fraction of constituent emitted to the air at time t (Equation from Table 5-7):

$$f = 1 - \frac{C_t}{C_o} = 1 - e^{-Kt/D} = 1 - e\ [-5.70\ (10^{-7})(86{,}400)/0.072]$$

$$= 1 - 0.50 = 0.50\quad .$$

5.2.7 Assumptions and Sensitivity Analyses

The RTI model incorporates the following assumptions to simplify development and use of the model:

- Volatilization and biodegradation are the predominant waste removal mechanisms (i.e., other mechanisms can be ignored).
- Waste is mixed uniformly within a surface layer of the soil.

- Waste does not flow as a liquid within the soil.
- The adsorption isotherm of a constituent is linear within the application surface layer and does not change with time.
- No bulk flow of gas is induced within the soil.
- The rate of biological decay/chemical reaction is a first-order process.
- The diffusion coefficient does not vary with either concentration or time.
- The concentration of a constituent in the gas phase at the surface of the soil is much lower than the concentration of that constituent in the gas phase within the soil.
- There is no diffusion of waste into the soil beneath the zone of incorporation.
- Liquid-vapor equilibrium is established at all times within the soil.

The RTI model was evaluated for sensitivity to each of the input parameters. In the analysis, each input parameter was varied over the entire range of reasonable values. The effect on emissions of parameter variations was noted, and the parameters showing the highest sensitivity were identified.

Individual constituent properties were found to have the most significant impact on land treatment emissions. These properties include vapor pressure, diffusivity in air, and biodegradation rate. The more volatile compounds are mostly emitted to the atmosphere unless a volatile compound also has a high biodegradation rate or low diffusivity. Compounds with low vapor pressures tend also to have lower diffusivities; thus, even if such compounds also have moderate or low biorates, they are mostly biodegraded rather than emitted to the air.

Operating and field parameters also have an impact on emissions but to a lesser extent than compound properties. Tilling depth, soil porosity, and waste loading all have an impact on air emissions, with the largest impact on the more volatile compounds. Tilling depth can have a substantial impact on air emissions of volatile compounds, especially if a compound also has a relatively high biorate. As tilling depth increases, materials remain in the soil for a longer time and thus have a greater chance of being biodegraded.

Waste loading can be varied in two ways: by increasing the concentration of a compound in the waste or by increasing the amount of material applied to the soil per unit area. If the concentration of a compound is changed, air emissions change in direct proportion to the change in concentration (i.e., the fraction of the compound that is emitted to the air remains constant). If total waste loading is changed, air emissions change in the same direction as the change in loading but not in direct proportion (i.e., the fraction emitted is lower for higher loading rates). These results assume that a treatment site is not overloaded to the point where biodegradation ceases to be a first-order process.

Average molecular weight of the oil has an effect on air emissions, but the magnitude of the effect is less than that of the other parameters studied. As average molecular weight goes up, the fraction emitted for a specific constituent increases; the fraction emitted decreases if the average molecular weight is reduced.

5.3 REFERENCES

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6.0 LANDFILLS AND WASTEPILES

6.1 INTRODUCTION

The main facilities in this category that constitute the model plants are waste fixation units, open landfills, closed landfills, and wastepiles.

All wastes that contain free liquids and that are destined for disposal in a landfill must be treated to eliminate the free liquids. This is often accomplished by adding a "fixative" to the waste, such as portland cement, cement kiln dust, or lime flue dust. These materials react with water in the waste and set up to form a dry material that encapsulates or binds the organic constituents of the waste. This fixation process is most often conducted in lined open pits or open tanks into which the liquid waste is poured. The fixative then is added and the materials are thoroughly mixed, most often with a backhoe. Alternatively, mechanical mixers such as pugmills can be used to blend the waste and fixative. Emissions are generated for as long as the waste remains in the pit. Emissions from this process may be estimated by using the open dump model.

A landfill is a facility, usually an excavated, lined pit, into which wastes are placed for permanent disposal. Emissions from open landfills, those still receiving wastes, can be estimated by applying the Research Triangle Institute (RTI) land treatment model.[1] Emissions from closed landfills, those filled to design capacity and with a cap (final cover) installed, can be estimated with the RTI closed landfill model.

Wastepiles are temporary accumulations of waste. They serve a storage function and have a limited life span. Emissions from wastepiles can be estimated by applying the RTI land treatment model.[2]

6.2 CLOSED LANDFILLS

6.2.1 Emission Model Equations

The RTI closed landfill model is used to estimate the time-dependent behavior of emissions from waste placed in a closed (capped) landfill that is vented to the atmosphere and (as a special case) open-landfill waste covered with daily earth covers. This model accounts for escape of the constituent of interest via two primary, independent mechanisms: diffusion through the cap and convective loss from barometric pumping through the vent(s). It is the purpose of this section to describe the model and its evolution in a general way and to present all model equations and major assumptions.

The model is based primarily upon the work of Farmer et al.,[3] who applied Fick's first law for steady-state diffusion to closed landfills. Farmer's equation utilizes an effective diffusion coefficient for the soil cap based on the work of Millington and Quirk.[4] A previous EPA study[5] was dedicated to the evaluation of available models for estimating emissions from hazardous waste treatment, storage, and disposal facilities (TSDF), including closed landfills. This study endorsed the models of Farmer et al.[6] and Thibodeaux[7] for closed landfills, apparently because of their treatment of soil-pore diffusion. Of the two, the Farmer et al.[8] model alone has received experimental verification (although to a limited degree) via a laboratory experiment using hexachlorobenzene-containing waste in a simulated landfill.

The diffusion model of Farmer et al.[9] was subsequently modified by RTI to allow for convective losses of the constituent of interest from the landfill, which can occur from barometric pumping. Furthermore, the decline in the emission rate from closed landfills over the long term was accounted for via the incorporation of a time-dependent decay function.

The barometric pumping emission mechanism results from changes in atmospheric pressure--as the pressure is lowered, gas flows out of the landfill through the vent(s) to equalize internal pressure. The contribution to total emissions resulting from barometric pumping equals the concentration of the constituent of interest in the gas within the landfill multiplied by the total flow of gas from the landfill. It is recognized that under certain conditions (e.g., the presence of significant biomass) biogas could be generated in a landfill. Biogas consists of methane and carbon dioxide, which is produced from the action of bacteria on organic material. Because of the convective or purging action of biogas in removing the constituent of interest in vapor form, biological decay (if it occurs) results in a net increase in the emission rate. However, it should be noted that there is no evidence that there is significant biomass (necessary for biogas generation) in any chemical waste landfill. Therefore, in this analysis it is assumed, as suggested in the literature, that the toxic property of the waste will inhibit biological processes and thus prevent biogas generation.[10] Hence, closed landfill model equations presented in this document account for diffusion through the cap and barometric pumping only.

The equations inherent in the RTI closed landfill model are as follows: Fick's first law for steady-state diffusion, based on the work of Farmer et al.,[11] for a landfill is given as:

$$J_i = -D_{ei}\ (C_{2i} - C_{si})/l \qquad (6\text{-}1)$$

where

J_i = vapor flux of the constituent through the soil surface, $g/cm^2 \cdot s$

D_{ei} = effective diffusion coefficient, cm^2/s

C_{2i} = concentration of constituent in the air above the cap, g/cm^3 air

C_{si} = concentration of the constituent in the vapor space beneath the cap, g/cm^3

l = cap thickness, cm.

(Because the concentration of the constituent at the surface is negligible, $C_{2i} \doteq 0$.)

Emissions associated with diffusion alone (E_{1i}, g/s) are obtained from the above equation by multiplying by the landfill surface area (A) in cm^2:

$$E_{1i} = J_i \times A\ . \qquad (6\text{-}2)$$

The effective diffusion coefficient of the constituent in soil, D_{ei}, is computed (using the expression developed by Millington and Quirk[12] and applied by Farmer et al.[13]) from the diffusion coefficient of the constituent in air, D_{ai}, as:

$$D_{ei} = D_{ai}\ (\epsilon_a^{3.33}/\epsilon_T^{2}) \qquad (6\text{-}3)$$

where

D_{ai} = vapor diffusion coefficient in air, cm^2/s

ϵ_a = soil cap air-filled porosity, cm^3/cm^3 (the actual air-filled porosity of the moist soil)

ϵ_T = total porosity of the soil cap.

The concentration of the constituent of interest in the vapor space beneath the cap is computed using the ideal gas law as follows:

$$C_{si} = P_i MW_i/RT' = P_i MW_i/R(T + 273) \qquad (6\text{-}4)$$

where

P_i = equilibrium partial pressure of constituent, atm

MW_i = molecular weight of constituent, g/g mol

R = gas constant, 82.05 $\frac{cm^3 \bullet atm}{K \bullet g\ mol}$

T' = absolute temperature in the landfill, K

T = temperature in the landfill, °C.

Calculation of the equilibrium partial pressure, P_i, depends on the type of waste liquid as follows:

a. For dilute aqueous solutions (where Henry's law applies), the equilibrium partial pressure of constituent within the landfill (P_i, atm) is computed as:

$$P_i = \frac{H_{ci} \rho_{liquid} X_i}{MW_{liquid}} \times 10^6 \frac{cm^3}{m^3} \qquad (6\text{-}5)$$

where

H_{ci} = Henry's law constant, $m^3 \bullet atm/mol$

ρ_{liquid} = density of waste liquid, g/cm^3 (1 g/cm^3 is generally a good estimate for this parameter)

X_i = mole fraction of constituent i in waste liquid

where

$$X_i = (C_i/MW_i)/[C_{H_2O}/18 + C_i/MW_i]$$

where

C_i = weight fraction of constituent i in the original waste liquid

C_{H_2O} = weight fraction of water in the original waste liquid

MW_{liquid} = average molecular weight of waste liquid, $\frac{g}{g\ mol}$.

b. For two-phase (water + organic liquid) or organic liquid waste, the equilibrium partial pressure of the constituent of interest within the landfill (P_i, atm) is computed using Raoult's law:

$$P_i = X_i P_i^* \qquad (6\text{-}6)$$

where

X_i = mole fraction of constituent in the organic liquid phase

where

$X_i = (C_i/MW_i)/[C_i/MW_i + C_{oil}/MW_{oil}]$

where

C_i = weight fraction of constituent i in the original waste liquid

C_{oil} = weight fraction of oil carrier-liquid in the original waste liquid

MW_{oil} = molecular weight of oil carrier-liquid, g/g mol

P_i^* = pure component vapor pressure of the constituent of interest, atm.

Emissions from barometric pumping are computed as:

$$E_{2i} = Q \times C_{si} \times A \qquad (6\text{-}7)$$

where

E_{2i} = emissions from barometric pumping, g/s

Q = flow rate of gas through the vent, expressed as a flux, cm^3/cm^2 landfill area•s

C_{si} = concentration of constituent in the gas within the landfill, g/cm^3 gas (see Equation (6-4))

A = surface area of the landfill, cm^2.

The gas flow rate, Q, is estimated using the following procedure.

a. Compute volume of gas available for barometric pumping, assuming the entire void-volume of the waste is available:

$$V_c = D \times A \times \epsilon_{fw} \tag{6-8}$$

where

V_c = volume of void space, cm^3

D = thickness of waste bed within landfill, cm

A = surface area of the landfill, cm^2.

ϵ_{fw} = air porosity fraction of fixed waste (dimensionless).

b. Compute the total volume of gas (cm^3) exiting the vent of the landfill due to changes in barometric pressure and/or temperature within the landfill:

$$V_B = V_C \left[\left(\frac{P_{ref}}{P_1}\right) \left(\frac{T_1 + 273}{T_{ref} + 273}\right) -1 \right] \tag{6-9}$$

where

V_B = total volume of gas exiting landfill, cm^3

P_{ref} = initial (reference) barometric pressure, mm Hg

P_1 = final barometric pressure, mm Hg

T_1 = final landfill temperature, °C

T_{ref} = initial (reference) landfill temperature, °C.

For cases in which $P_1 > P_{ref}$ and/or $T_1 < T_{ref}$, the computed value of V_B may be negative (indicating a condition of gas flow into the landfill). Because this condition results in no emissions associated with barometric pumping, V_B should be set equal to zero to avoid calculational errors in the following steps.

c. Compute the average flow rate of gas from the landfill over the time interval of interest:

$$Q = \frac{V_B}{\Delta t\ A} \tag{6-10}$$

where

Q = average flow rate of gas from the vent due to barometric pumping, cm^3/cm^2 landfill area•s

Δt = time interval over which the change in pressure and/or temperature occurred, s

A = landfill area, cm^2.

In an average day, barometric pressure drops 4 mbar from a typical value of 1,013 mbar. Landfill temperature is assumed to remain constant. Hence, under these conditions, P_{ref} = 1,013 mbar, P_1 = 1,009 mbar, $T_{ref} = T_1$ = 15 °C, and $\Delta t = 8.64 \times 10^4$ s.

Having computed the instantaneous emissions associated with diffusion through the cap and barometric pumping, the total initial emission rate at the time of landfill closure, E_i^* (g/s), is computed as the sum:

$$E_i^* = E_{1i} + E_{2i} \quad . \tag{6-11}$$

The total instantaneous emission rate at any time then is computed via an exponential decay function:

$$E_i(t) = \frac{(3{,}600\ s/h)(24\ h/d)(365.25\ d/yr)E_i^*}{10^6} \exp\,(-\lambda t)$$

$$E_i(t) = 31.56\ E_i^* \exp\,(-\lambda t) \tag{6-12}$$

where

$E_i(t)$ = total time-dependent emission rate, Mg/yr

E_i^* = initial emission rate, at time of landfill closure, g/s

t = time since landfill closure, mo

λ = "decay" constant, mo^{-1}.

The "decay" constant, λ, is computed as follows:

$$\lambda = \frac{(3{,}600 \text{ s/h}) \times (24 \text{ h/d}) \times 365.25 \text{ d/yr}) \times E_i^*}{12 \text{ mo/yr} \times M_{oi}}$$

$$\lambda = 2.63 \times 10^6 \; E_i^*/M_{oi} \qquad (6\text{-}13)$$

where M_{oi} is the total mass of the constituent of interest in the landfill (g). This parameter can be computed from the weight fraction of the constituent in the original waste liquid (C_i), the mass of original waste liquid in a unit volume of fixed waste (W), the landfill surface area (A), and the thickness of the waste layer within the landfill (D):

$$M_{oi} = C_i \; W \; A \; D \quad . \qquad (6\text{-}14)$$

The average emission rate from a closed, vented landfill over the time since landfill closure is equal to the integral of the emission rate equation over the time period divided by the time period, which yields the following expression:

$$E_{Ai}(t) = \frac{(3{,}600 \text{ s/h})(24 \text{ h/d})(365.25 \text{ d/yr}) \; E_i^*}{(10^6 \text{ g/Mg})\lambda t} \left[1 - e^{-\lambda t}\right]$$

$$E_{Ai}(t) = \frac{31.56 E_i^*}{\lambda t} \left[1 - e^{-\lambda t}\right] \qquad (6\text{-}15)$$

where

$E_{Ai}(t)$ = average emission rate over the time since landfill closure, Mg/yr

t = time since landfill closure, mo.

Table 6-1 summarizes the equations necessary to apply the RTI closed landfill model.

The model is highly sensitive to the air porosity of the clay cap (ϵ_a), which largely determines the diffusion rate through the cap. The model is sensitive to the properties of the constituent of interest, particularly the vapor pressure (P_i^*), Henry's law constant (H_{ci}), and mole fraction in the waste liquid (X_i). Because temperature affects volatility, the model is sensitive to temperature. Other parameters to which the model is sensitive include the depth of the fixed waste (D), the air porosity of the fixed waste (ϵ_{fw}), the landfill surface area (A), and the barometric pressure change ($P_{ref} - P_1$). This latter group of parameters is significant in that it impacts the barometric pumping rate or the volume of gas available for pumping. In contrast to these parameters, the model exhibits relatively low sensitivity to the diffusivity of the constituent in air (D_{ai}), the cap thickness (l), and the total mass of the constituent in the landfill (M_{oi}).

The major assumptions associated with the RTI closed landfill model are as follows:

- The liquid waste containing the constituent of interest is assumed to be bound in the fixed waste within the landfill.
- The constituent of interest in the gas within the landfill is assumed to be in equilibrium with the liquid in the waste.
- Adsorption of the constituent of interest onto the soil of the cap is assumed to be negligible.
- The fraction of air-filled space in the landfill cap (air porosity) is assumed to remain relatively constant over the long term.
- The effective diffusion coefficient of the cap is assumed not to vary with either the concentration of the constituent of interest or time.
- The concentration of the constituent of interest in air at the top of the landfill cap is assumed to be effectively 0.
- No biodegradation (with concurrent production of biogas) is assumed to occur due to the suppression of biological processes by the toxic waste.

TABLE 6-1. RTI CLOSED LANDFILL MODEL

$$E_i(t) = 31.56\ E_i^* \exp(-\lambda t)$$

$$E_{Ai}(t) = \frac{31.56\ E_i^*}{\lambda t} \left[1 - e^{-\lambda t}\right]$$

$$\lambda = 2.63 \times 10^6\ E_i^*/M_{oi}$$

$$M_{oi} = C_i\ W\ A\ D$$

$$E_i^* = E_{1i} + E_{2i}$$

$$E_{1i} = J_i \times A$$

$$J_i = -D_{ei}\ (C_{2i} - C_{si})/1$$

$$D_{ei} = D_{ai}\ ({\epsilon_a}^{3.33}/{\epsilon_T}^2)$$

$$C_{2i} = 0$$

$$C_{si} = P_i\ MW_i/R\ (T + 273)$$

$$P_i = \frac{H_{ci}\ \rho_{liquid}\ X_i}{MW_{liquid}} \times 10^6\ \frac{cm^3}{m^3}$$ (dilute aqueous waste liquids)

$$X_i = (C_i/MW_i)/(C_{H_2O}/18 + C_i/MW_i)$$ (dilute aqueous waste liquids)

$$P_i = X_i\ P_i^*$$ (two-phase liquid or organic liquid waste)

$$X_i = (C_i/MW_i)/(C_i/MW_i + C_{oil}/MW_{oil})$$ (two-phase liquid or organic liquid waste)

$$E_{2i} = Q\ C_{si}\ A$$

$$Q = V_B/(\Delta t\ A)$$

$$V_B = V_C \left[\left(\frac{P_{ref}}{P_1} \right) \left(\frac{T_1 + 273}{T_{ref} + 273} \right) - 1 \right]$$

$$V_C = D\ A\ \epsilon_{fw}$$

(continued)

TABLE 6-1 (continued)

Variable	Definition	Data source
A	Landfill surface area, cm^2	Westat survey[a]
C_{si}	Concentration of constituent i in the gas within the landfill, g/cm^3 gas	Calculated
C_{2i}	Concentration of constituent i in air above the cap, g/cm^3	Assumed
C_i	Weight fraction of constituent i in the original waste liquid (dimensionless)	Definition
C_{H_2O}	Weight fraction of water in the original waste liquid (dimensionless)	Definition
C_{oil}	Weight fraction of oil carrier-liquid in the original waste liquid (dimensionless)	Definition
D	Thickness of waste bed within landfill, cm	Westat survey[b]
D_{ai}	Diffusivity of constituent i in air, cm^2/s	Literature
D_{ei}	Effective diffusion coefficient of constituent i in clay cap, cm^2/s	Calculated
$E_{Ai}(t)$	Average emission rate of constituent i over time t since landfill closure, Mg/yr	Calculated
$E_i(t)$	Total instantaneous emission rate of constituent i at time t since landfill closure, Mg/yr	Calculated
E_i^T	Total initial emission rate of constituent i at time of landfill closure, g/s	Calculated
E_{1i}	Initial emission rate of constituent i at landfill closure due to diffusion alone, g/s	Calculated

[a] Reference 14.
[b] Reference 15.

(continued)

TABLE 6-1 (continued)

Variable	Definition	Data source
E_{2i}	Initial emission rate of constituent i at landfill closure due to barometric pumping alone, g/s	Calculated
H_{ci}	Henry's law constant for constituent i, $m^3 \bullet atm/mol$	Literature
J_i	Initial diffusion flux of constituent i, $g/cm^2 \bullet s$	Calculated
l	Landfill cap thickness, cm	Literature
M_{oi}	Initial mass of constituent i in the landfill, g	Definition or calculated
MW_i	Molecular weight of constituent i, g/g mol	Literature
MW_{liquid}	Average molecular weight of the dilute aqueous waste liquid, g/g mol (assumed to be 18 g/g mol)	Estimated
MW_{oil}	Molecular weight of the oil carrier-liquid, g/g mol	Definition or estimated
P_i^*	Pure component vapor pressure of constituent i, atm	Literature
P_i	Equilibrium partial pressure of constituent i in the vapor space, atm	Calculated
P_{ref}	Initial (reference) barometric pressure, mm Hg	Meteorological information
P_1	Final barometric pressure after Δt, mm Hg	Meteorological information
Q	Average flow rate of gas from landfill vent(s) due to barometric pumping, cm^3/cm^2 landfill area$\bullet$s	Calculated
R	Ideal gas constant, 82.05 $cm^3 \bullet atm/g\ mol \bullet K$	Literature
t	Time since landfill closure, mo	Definition

(continued)

TABLE 6-1 (continued)

Variable	Definition	Data source
Δt	Time interval used to determine average barometric pumping rate, s	Definition
T	Temperature within landfill, °C	Estimated from literature data
T_{ref}	Initial (reference) landfill temperature, °C	Estimated from literature data
T_1	Final landfill temperature after Δt, °C	Estimated
V_B	Total volume of gas exiting landfill in Δt, cm^3	Calculated
V_C	Total volume of void space within waste, cm^3	Calculated
W	Mass of original waste liquid in a unit volume of fixed waste, g/cm^3	Definition or estimated
X_i	Mole fraction of constituent i in the aqueous liquid (for dilute aqueous waste) or in the organic phase (for two-phase or organic liquid waste) (dimensionless)	Definition
ϵ_a	Air porosity of the clay cap (dimensionless)	Estimated from clay property data
ϵ_T	Total porosity of the clay cap (dimensionless)	Estimated from clay property data
ϵ_{fw}	Air porosity of the fixed waste (dimensionless)	Estimated from fixed waste property data
ρ_{liquid}	Density of dilute aqueous waste liquid, g/cm^3 (generally equals 1 g/cm^3)	Definition or estimated
λ	Exponential decay constant, mo^{-1}	Calculated

- The landfill is assumed to be vented to the atmosphere. The volume of gas available for barometric pumping is assumed to consist of the total void-volume of the waste bed.
- No transport of the constituent of interest in moving water is assumed to occur.

6.2.2 Model Plant Parameters for Closed Landfills

The characteristics of a model closed landfill facility are discussed here. This model facility is used as the basis for an example calculation in Section 6.2.3.

The model facility for closed landfills has an area of 1.417×10^8 cm^2 (3.5 acres). This value represents an approximately midrange value from the Westat survey.[16] A reasonable value of landfill depth, also selected from the Westat survey,[17] is 458 cm (15 ft). The landfill cap is assumed to be composed of compacted clay. The cap thickness value of 107 cm (3.5 ft) represents the average of extremes in thickness of clay caps reported in site studies (2 ft to 6 ft).[18] The value used for air porosity of the clay cap is 0.08 (8 percent), while the total porosity is 0.41 (41 percent). These values were computed based on reasonable physical properties and level of compaction for compacted clay.[19] The landfill is assumed to be vented to the atmosphere. The temperature beneath the landfill cap is estimated at 15 °C, which represents the temperature of shallow ground water at a midlatitude U.S. location.[20] This temperature is assumed to remain constant. The landfill is assumed to be exposed to a nominal barometric pressure of 1,013 mbar, which represents an estimate of the annual average atmospheric pressure in the United States.[21] Barometric pumping is estimated for the landfill using a daily pressure drop from the nominal value of 4 mbar. The 4 mbar value represents an estimate of the annual average diurnal pressure drop.[22]

The model closed landfill facility is assumed to contain fixed waste. The waste liquid (before fixation) selected for the facility is assumed to be a two-phase aqueous/organic containing 20 percent chloroform, 20 percent low-volatility organic,* and 60 percent water (by weight). This liquid has an average density of 1.16 g/cm^3. The fixation industry indicates that waste liquid, when combined with fixative, may in actuality increase in volume by as much as 50 percent.[23,24] The volume change, which is a function of the specific waste being fixed and the specific formulation of the fixative, can only be determined experimentally. In view of the inherent variability in the fixation process and the lack of real data, for the purpose of this calculation the assumption is made that the fixation process does not change the waste volume. This assumption is environmentally conservative and may result in an overestimation of the landfill emissions. Actual volume changes that may take place as a result of fixation can easily be accounted for because the change in the calculated emissions is inversely proportional to the change in waste volume. One industry contact indicated that, for the purposes of estimating emissions, the assumption of no volume change during fixation was reasonable.[25] Based on the waste liquid density and the assumption of no volume increase from fixation, the mass of waste liquid in a unit volume of fixed waste is 1.16 g/cm^3. The air porosity of the fixed waste (used to estimate the total volume of gas available for barometric pumping) is taken to be 0.25 (25 percent). This value was inferred from measurements of total porosity and moisture content of various fixed wastes,[26] and, for the purposes of this analysis, is assumed to pertain to waste within the landfill as opposed to waste immediately following fixation. As discussed previously, there is no evidence for significant biomass in any chemical waste landfill. Therefore, in this analysis it is assumed, as suggested in the literature, that the toxic property of the waste will inhibit biological processes and thus prevent biogas generation.[27] Hence, the waste biomass concentration is taken to be 0 g/cm^3.

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*For modeling purposes, this component of the waste liquid represents the oil carrier-liquid.

The properties of chloroform that are pertinent to this analysis include the molecular weight (119.4 g/g mol), pure component vapor pressure at 15 °C (0.162 atm), diffusivity in air at 15 °C (0.10 cm^2/s) and density (1.49 g/cm^3). The low-volatility organic liquid present in the waste has a molecular weight of 147 g/g mol and a density of 1.31 g/cm^3.

Table 6-2 summarizes the model facility parameters for closed landfills used in the example calculation in Section 6.2.3.

TABLE 6-2. INPUT PARAMETERS--CLOSED LANDFILL

Parameter	Value
Area	1.417×10^8 cm^2 (3.5 acres)
Waste bed thickness	457 cm (15 ft)
Cap thickness	107 cm (3.5 ft)
Cap air porosity	0.08 (8%)
Cap total porosity	0.41 (41%)
Type landfill	Vented
Temperature beneath cap	15 °C
Typical barometric pressure	1,013 mbar
Daily barometric pressure drop	4 mbar
Waste liquid (before fixation)	Two-phase aqueous/organic
Liquid composition	20% chloroform, 20% low-volatility organic (oil), 60% water (by weight)
Liquid/fixative	1 unit volume liquid + dry fixative = 1 unit volume fixed waste
Liquid in fixed waste	1.16 g/cm^3
Air porosity fixed waste	0.25 (25%)
Biomass concentration	0 g/cm^3
Chloroform properties	
Molecular weight	119.4 g/g mol
Vapor pressure (15 °C)	0.162 atm (123 mm Hg)
Diffusivity in air (15 °C)	0.10 cm^2/s
Density	1.49 g/cm^3
Low-volatility organic[a] properties	
Molecular weight	147 g/g mol
Density	1.31 g/cm^3

[a] Also referred to as oil "carrier-liquid."

6.2.3 Example Calculation for Closed Landfill

This section presents a step-by-step calculation of emissions from a closed landfill that is vented to the atmosphere. The equations discussed in Section 6.2.1 and summarized in Table 6-1 are used with the model unit parameters in Section 6.2.2 to estimate emissions from a fixed, two-phase aqueous/organic waste containing chloroform:

- Waste liquid (before fixation): 20 percent chloroform, 20 perpercent low-volatility organic liquid, 60 percent water (by weight)
- Liquid/fixative: 1 unit volume liquid + dry fixative = 1 unit volume fixed waste
- Waste biomass concentration: 0 g/cm^3
- Landfill area: 1.417×10^8 cm^2 (3.5 acres)
- Waste bed thickness: 457 cm (15 ft)
- Cap thickness: 107 cm (3.5 ft)
- Type landfill: vented
- Temperature beneath cap: 15 °C
- Time period for emission calculation: 1 yr.

a. Compute the effective diffusion coefficient, D_{ei} (cm^2/s) (Equation (6-3)):

$$D_{ei} = D_{ai}(\epsilon_a^{3.33}/\epsilon_T^{2})$$

$$D_{ei} = (0.10\ \text{cm}^2/\text{s})\ (0.08)^{3.33}/(0.41)^2$$

$$D_{ei} = 1.32 \times 10^{-4}\ \text{cm}^2/\text{s}\ .$$

b. Compute the equilibrium partial pressure of chloroform in the vapor space, P_i (atm):

The waste before fixation was a two-phase liquid. Hence, Raoult's law applies. The mole fraction for this case is computed as:

$$X_i = (C_i/MW_i)/(C_i/MW_i + C_{oil}/MW_{oil})$$

X_i = (0.20/119.4 g/g mol) ÷ [0.20/119.4 g/g mol + 0.20/147 g/g mol]

X_i = 0.55 .

From Raoult's law (Equation (6-6)):

$P_i = X_i P_i^*$

P_i = (0.55)(0.162 atm)

$P_i = 8.91 \times 10^{-2}$ atm .

c. Compute the concentration of chloroform in the vapor space beneath the cap, C_{si} (g/cm^3 void space) (Equation (6-4)):

$C_{si} = P_i MW_i/R(T + 273)$

$$C_{si} = \frac{(8.91 \times 10^{-2}\ \text{atm})(119.4\ \text{g/g mol})}{(82.05\ \text{cm}^3\bullet\text{atm/g mol}\bullet\text{K})\ (15 + 273)}$$

$C_{si} = 4.50 \times 10^{-4}$ g/cm^3 .

d. Compute initial chloroform emission flux resulting from diffusion through the cap only, J_i (g/cm$^2\bullet$s) (Equation (6-1)):

$J_i = -D_{ei}(C_{2i} - C_{si})/l$

$J_i = -(1.32 \times 10^{-4}\ \text{cm}^2/\text{s})(0\ \text{g/cm}^3 - 4.50 \times 10^{-4}\ \text{g/cm}^3)/107\ \text{cm}$

$J_i = 5.55 \times 10^{-10}$ g/cm$^2\bullet$s .

e. Compute initial chloroform emissions resulting from diffusion through the cap only, E_{1i} (g/s) (Equation (6-2)):

$E_{1i} = J_i \times A$

$E_{1i} = (5.55 \times 10^{-10}\ \text{g/cm}^2\bullet\text{s})(1.417 \times 10^8\ \text{cm}^2)$

$E_{1i} = 7.86 \times 10^{-2}$ g/s .

f. Estimate the barometric pumping-induced gas flow rate through the vent(s):

1. Compute the volume of gas available for barometric pumping, V_c (cm^3) (Equation (6-8)):

$$V_c = D \times A \times \epsilon_{fw}$$

$$V_c = (457\ cm)(1.417 \times 10^8\ cm^2)(0.25)$$

$$V_c = 1.62 \times 10^{10}\ cm^3 \quad .$$

2. Compute volume of gas exiting the vent due to barometric pressure change, V_B (cm^3) (Equation (6-9)):

$$V_B = V_c \left[\left(\frac{P_{ref}}{P_1}\right) \left(\frac{T_1 + 273}{T_{ref} + 273}\right) - 1 \right] \quad .$$

For this case, $T_1 = T_{ref} = 15\ °C$, and barometric pressure drops by 4 mbar from the nominal value of 1,013 mbar:

$$V_B = 1.62 \times 10^{10}\ cm^3 \left[\left(\frac{1{,}013\ mbar}{1{,}009\ mbar}\right) \left(\frac{15\ °C + 273\ K}{15\ °C + 273\ K}\right) - 1 \right]$$

$$V_B = 6.42 \times 10^7\ cm^3 \quad .$$

3. Compute the average flow rate of gas over the time interval, Q (cm^3/cm^2 landfill area • s) (Equation (6-10)):

The average diurnal pressure drop of 4 mbar occurs within a 24-h period. For convenience, the gas flow from this pressure change is averaged over 24 h (equals 8.64×10^4 s).

$$Q = \frac{V_B}{\Delta t A}$$

$$Q = \frac{6.42 \times 10^7 cm^3}{(8.64 \times 10^4\ s)(1.417 \times 10^8\ cm^2)}$$

$$Q = 5.25 \times 10^{-6}\ cm^3/cm^2 \bullet s \quad .$$

4. Compute the barometric pumping-induced emission rate, E_{2i} (g/s) (Equation (6-7)):

$$E_{2i} = Q \times C_{si} \times A$$

$$E_{2i} = (5.25 \times 10^{-6}\ \text{cm}^3/\text{cm}^2\bullet\text{s})(4.50 \times 10^{-4}\ \text{g/cm}^3)(1.417 \times 10^8\ \text{cm}^2)$$

$$E_{2i} = 0.335\ \text{g/s} \quad .$$

g. Compute the total initial emission rate, E_i^* (g/s) (Equation (6-11):

$$E_i^* = E_{1i} + E_{2i}$$

$$E_i^* = 7.86 \times 10^{-2} + 0.335$$

$$E_i^* = 0.413\ \text{g/s} \quad .$$

h. Compute the time-dependent instantaneous emission rate:

1. Compute total mass of constituent i in landfill, M_{oi}:

First compute W, the mass of original waste liquid in a unit volume of fixed waste. Assuming one unit volume of waste liquid results in one unit volume of fixed waste, this parameter can be computed using the densities of the waste liquid components and their weight fractions as follows:

$$W = [(1.49\ \text{g/cm}^3)(0.2) + (1.31\ \text{g/cm}^3)(0.2) + (1\ \text{g/cm}^3)(0.6)]$$

$$\times\ 1\ \text{cm}^3\ \text{liquid/cm}^3\ \text{fixed waste}$$

$$= 1.16\ \text{g/cm}^3 \quad .$$

M_{oi} is then computed as:

$$M_{oi} = C_i\ W\ A\ D$$

$$M_{oi} = \frac{20\ \text{g chloroform}}{100\ \text{g liquid}} \times \frac{1.16\ \text{g liquid}}{\text{cm}^3\ \text{fixed waste}} \times 1.417 \times 10^8\ \text{cm}^2$$

$$\times\ 457\ \text{cm} = 1.50 \times 10^{10}\ \text{g chloroform} \quad .$$

2. Compute the decay constant, λ (mo^{-1}) (Equation (6-13)):

$$\lambda = 2.63 \times 10^{6}\ E_i^*/M_{oi}$$

$$\lambda = (2.63 \times 10^{6})(0.413\ g/s)/1.50 \times 10^{10}\ g$$

$$\lambda = 7.25 \times 10^{-5}\ mo^{-1}\ .$$

3. Compute the instantaneous emission rate, E_i, in Mg/yr, after 1 yr (Equation (6-12)):

$$E_i(t) = 31.56\ E_i^*\ \exp(-\lambda t)$$

$$E_i = (31.56)(0.413\ g/s)\ \exp(-7.25 \times 10^{-5}\ mo^{-1} \times 12\ mo)$$

$$E_i = 13.0\ Mg/yr\ \ .$$

i. Compute the average emission rate in the first year, E_{Ai}, in Mg/yr (Equation (6-15)):

$$E_{Ai}(t) = \frac{31.56\ E_i^*}{\lambda t}\left[1 - e^{-\lambda t}\right]$$

$$E_{Ai} = \frac{(31.56)(0.413\ g/s)}{(7.25 \times 10^{-5}\ mo^{-1})\ (12\ mo)}\left[1\text{-}\exp\left[-12\ mo \times 7.25 \times 10^{-5}\ mo^{-1}\right]\right]$$

$$E_{Ai} = 13.0\ Mg/yr\ \ .$$

6.3 FIXATION PITS

6.3.1 Emission Model Equations

The open dump model is used to estimate air emissions of the constituent of interest from open waste sources that, for the duration of the emission calculation, may be considered to have an effectively constant concentration of the constituent of interest in the waste surface layer. An example of such sources is waste fixation pits (the fixation operation is of short duration, approximately 2 h, and includes stirring the mixture).

It is the purpose of this section to describe the model, its history, and inherent assumptions.

A previous EPA study[28] that identified and evaluated models for estimating emissions from hazardous waste TSDF identified only one model (the open dump model) pertaining directly to uncovered waste. The open dump model is based originally upon the work of Arnold,[29] who applied unsteady-state diffusion theory to the case of diffusion into still air at constant pressure from a liquid surface at which the concentration of a volatilizing liquid remained constant. Convection was assumed to be absent. (This configuration, referred to as the "semi-infinite column," can be approximated in practice by the vaporization of a liquid into a cylinder of sufficient height such that vapor does not reach the top during the experiment.) Arnold's solution provided the cumulative vapor release from the surface as a function of time. Arnold noted, however, that the Fick's law solution was not rigorously correct because Fick's law does not account for the displacement of the inert gaseous medium (air) by the volatilizing vapor. Arnold thus presented the Fick's law solution with a correction factor (derived from a more rigorous treatment) to account for this effect:

$$V = 2y^*A\sqrt{\frac{Dt}{\pi F_v}} \tag{6-16}$$

where

V = volume of vapor released at ambient pressure and temperature, cm^3

y^* = equilibrium mole fraction of the volatilizing constituent in the gas phase at the liquid-gas interface

A = area of the liquid surface, cm^2

D = diffusivity of volatilizing constituent in air, cm^2/s

t = time, s

F_v = correction factor for Fick's law

π = 3.1416.

The correction factor, F_v, is dependent solely upon y^*. It is presented in tabular form in Table 6-3 and in graphical form in Figure 6-1.

TABLE 6-3. FICK'S LAW CORRECTION FACTOR[30] AS A FUNCTION OF y^*

y^*	F_v
0	1
0.05	0.9635
0.10	0.9268
0.15	0.8900
0.20	0.8527
0.25	0.8152
0.30	0.7774
0.35	0.7391
0.40	0.7004
0.45	0.6613
0.50	0.6215
0.55	0.5810
0.60	0.5398
0.65	0.4976
0.70	0.4540
0.75	0.4088
0.80	0.3616
0.85	0.3112
0.90	0.2546
0.95	0.1893
1	0

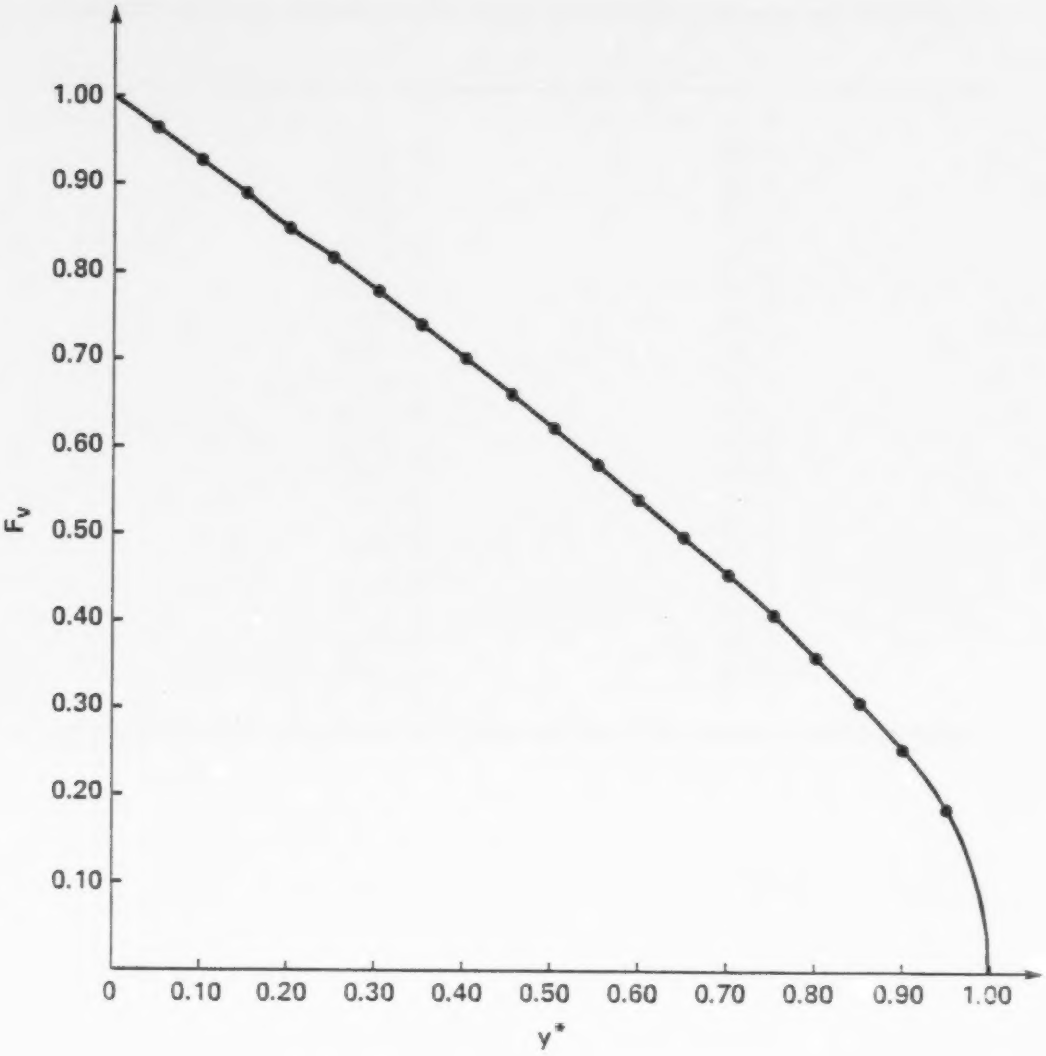

Figure 6-1. Fick's law correction factor F_v as a function of y^*.[31]

The equation was subsequently modified,** as indicated by Shen,[32] to yield an expression for the average rate of vapor release in terms of windspeed. Shen generalized the expression to account for more than one constituent in the liquid through the incorporation of a weight fraction term for the constituent of interest. (Subsequent analysis indicates that this term is expressed more accurately as a mole fraction of the constituent of interest.)

The resulting equation may thus be expressed as:

$$\left.\frac{dV_i}{dt}\right|_{avg} = 2y_i^* w \sqrt{\frac{D_i l U}{\pi F_v}} \qquad (6\text{-}17)$$

where

$\left.\frac{dV_i}{dt}\right|_{avg}$ = average emission rate of the constituent of interest from the surface at ambient pressure and temperature, cm^3/s

y_i^* = equilibrium mole fraction of the i-th constituent in the gas phase

w = width of volatilizing surface perpendicular to the wind direction, cm

l = length of volatilizing surface, parallel to the wind direction, cm

U = windspeed, cm/s.

The calculation of y_i^* varies (for a multicomponent liquid), depending upon whether volatilization from the liquid is governed by Raoult's law or Henry's law. If Raoult's law applies (i.e., if the waste is a two-phase liquid or an organic liquid):

$$y_i^* = X_i P_i^* / P_o \qquad (6\text{-}18)$$

**Modifications included (1) taking the time derivative (to produce a rate expression), (2) making a change of variables by substituting $t = x/U$ (an expression for time expressed in terms of position "x" along the length of the dump and windspeed U), and (3) integrating along the length of the surface to yield the total emission rate. The change of variables represents an attempt to deal with convective air flow.

where

X_i = mole fraction of the i-th constituent in the organic phase

where

$X_i = (C_i/MW_i)/[C_i/MW_i + C_{oil}/MW_{oil}]$

where

C_i = weight fraction of constituent i in the original waste liquid

MW_i = molecular weight of constituent i, g/g mol

C_{oil} = weight fraction of oil carrier-liquid in the original waste liquid

MW_{oil} = molecular weight of oil carrier-liquid (g/g mol)

P_i^* = pure component vapor pressure of the i-th constituent, mm Hg

P_o = atmospheric pressure, mm Hg.

If Henry's law applies:

$$y_i^* = 55{,}555\ X_i H_{ci} \tag{6-19}$$

where

X_i = mole fraction of constituent i in the aqueous liquid

where

$X_i = (C_i/MW_i)/[C_{H_2O}/18 + C_i/MW_i]$

where

C_i = weight fraction of constituent i in the original waste liquid

C_{H_2O} = weight fraction of water in the original waste liquid

MW_i = molecular weight of constituent i, g/g mol

H_{ci} = Henry's law constant for the i-th constituent in the liquid, $m^3 \cdot atm/mol$

55,555 = conversion factor, g mol water/m^3.

The volumetric emission rate (cm^3/s) presented in Equation (6-17) pertains to the pure constituent of interest only (per the principle of partial volumes) at ambient pressure (total pressure) and temperature. The mass emission rate of the constituent of interest may be obtained by multiplying by its gas density, as computed from the ideal gas law:

$$\rho_i = \frac{P_o MW_i}{RT} \qquad (6\text{-}20)$$

where

ρ_i = gas density of the pure constituent of interest at system pressure and temperature

P_o = total system pressure (ambient pressure), mm Hg

MW_i = molecular weight of constituent i, g/g mol

R = ideal gas constant, 62,300 mm Hg•cm^3/g mol•K

T = ambient temperature, K.

The open dump equation in its final form is thus presented as:

$$E_i = \frac{2P_o MW_i y_i^* w}{RT} \sqrt{\frac{D_i l U}{\pi F_v}} \qquad (6\text{-}21)$$

where

E_i = emission rate of the constituent of interest from the emitting surface, g/s.

Table 6-4 summarizes the model equations.

The open dump model is quite sensitive to the pure component vapor pressure (P_i^*) or Henry's law constant (H_i) for the constituent of interest, the mole fraction of the constituent in the waste (X_i), the molecular weight of the constituent (MW_i), the width of the pit (w) (assumed to be in the direction perpendicular to the wind flow), and the ambient temperature (T). However, because of the wide range of likely values for parameters such as vapor pressure, Henry's law constant, mole fraction of the constituent in the waste, and temperature, these four parameters may have the greatest impact on model sensitivity.

TABLE 6-4. OPEN DUMP MODEL

Emission rate equations

$$E_i = \frac{2\ P_o\ MW_i\ y_i^* w}{RT} \sqrt{\frac{D_i l U}{\pi\ F_v}}$$

$y_i^* = 55{,}555\ X_i H_{ci}$ (dilute aqueous waste); $y_i^* = \frac{X_i\ P_i^*}{P_o}$ (two-phase liquid or organic liquid waste)

$X_i = (C_i/MW_i)/(C_{H_2O}/18 + C_i/MW_i)$ (dilute aqueous waste liquids)

$X_i = (C_i/MW_i)/(C_i/MW_i + C_{oil}/MW_{oil})$ (two-phase liquid or organic liquid waste)

Variable	Description	Data source
E_i	Emission rate of constituent i, g/s	Calculated
y_i^*	Equilibrium mole fraction of constituent i in the gas phase (dimensionless)	Calculated
P_o	Atmospheric pressure, mm Hg	Literature
MW_i	Molecular weight of constituent i, g/g mol	Data base
MW_{oil}	Molecular weight of oil carrier-liquid in the original waste liquid, g/g mol	Definition or estimated
l	Length of dump in the direction of wind flow, cm	Definition
C_i	Weight fraction of constituent i in the waste liquid (dimensionless)	Definition
C_{H_2O}	Weight fraction of water in the original waste liquid (dimensionless)	Definition
C_{oil}	Weight fraction of oil in the original waste liquid (dimensionless)	Definition
w	Width of dump in the direction perpendicular to the wind flow, cm	Definition
P_i^*	Pure component vapor pressure of constituent i, mm Hg	Data base
R	Universal gas constant, 62,300 mm Hg•cm^3/g mol•K	Literature

(continued)

TABLE 6-4 (continued)

Variable	Description	Data source
X_i	Mole fraction of constituent i in the aqueous liquid (for dilute aqueous waste) or in the organic phase (for two-phase or organic liquid waste) (dimensionless)	Calculated
D_i	Diffusivity of constituent i in air, cm^2/s	Data base
U	Windspeed, cm/s	Definition
T	Temperature, K	Definition
H_{ci}	Henry's law constant for constituent i, $atm \cdot m^3/g$ mol	Literature
F_v	Fick's law correction factor (a function of y_i^*)	Tabulated

The model exhibits significantly lower sensitivity to the following parameters: windspeed (U), diffusion coefficient of constituent (D_i), Fick's law correction factor (F_v), and length of the pit (l) (assumed to be in the direction parallel to the wind flow).

The major assumptions associated with the open dump model are as follows:

- Waste liquid (containing the constituent of interest) is present at the surface of the dump at all times. For two-phase aqueous/organic waste, the organic phase is assumed to cover the entire surface of the dump.
- The concentration of the constituent of interest at the surface does not decrease over the duration of the time period of interest.
- No convection boundary layer is present at the surface of the dump.

6.3.2 Model Plant Parameters for Fixation Pits

The characteristics of a model fixation pit are discussed here. This model facility is used as the basis for an example calculation in Section 6.3.3.

The model fixation pit has a length of 610 cm (20 ft), a width of 305 cm (10 ft), and a depth of 305 cm (10 ft). These dimensions represent reasonable estimates of industry practice based on observations at actual sites. The duration of the fixation operation is taken to be a maximum of 2 h, based on operating practice at one site.[33]

Meteorological conditions needed as input parameters include ambient temperature and windspeed. For this analysis, a standard temperature of 25 °C and windspeed of 447 cm/s (10 mi/h) are used. The wind direction is assumed to be along the length of the pit.

The waste liquid selected for this model facility is assumed to be a two-phase aqueous/organic containing 20 percent chloroform, 20 percent low-volatility oil,* and 60 percent water (by weight). The properties of chloroform that are pertinent to this analysis include the molecular weight

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*For modeling purposes, this component of the waste liquid represents the oil carrier-liquid.

(119.4 g/g mol), pure component vapor pressure (208 mm Hg), and diffusivity in air (0.104 cm^2/s). The low-volatility organic liquid present in the waste has a molecular weight of 147 g/g mol.

Table 6-5 summarizes the model facility parameters for fixation pits used in the example calculation in Section 6.3.3.

6.3.3 Example Calculation for Fixation Pit

This section presents a step-by-step calculation of emissions from a fixation pit. The equations discussed in Section 6.3.1 and summarized in Table 6-4 are used with the model unit parameters in Section 6.3.2 to estimate emissions associated with fixation of a two-phase aqueous/organic waste containing chloroform:

- Waste liquid: 20 percent chloroform, 20 percent low-volatility organic liquid, 60 percent water (by weight)
- Length of pit: 610 cm (20 ft)
- Width of pit: 305 cm (10 ft)
- Windspeed: 447 cm/s (10 mi/h)
- Wind direction: along length of pit
- Temperature: 25 °C*
- Duration of process: 7,200 s (2 h).

a. Compute the mole fraction of chloroform, X_i:

The waste liquid is two-phase, the organic phase having equal parts by weight of chloroform and low-volatility oil (50 percent each). Hence, Raoult's law applies:

$$X_i = (C_i/MW_i)/[C_i/MW_i + C_{oil}/MW_{oil})$$

$$X_i = (0.20/119.4 \text{ g/g mol}) \div (0.20/119.4 \text{ g/g mol} + 0.20/147 \text{ g/g mol})$$

$$X_i = 0.55 \quad .$$

b. Compute the equilibrium mole fraction of chloroform in the gas phase, y_i^*:

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*Temperature may be elevated by exothermic reactions during mixing.

TABLE 6-5. INPUT PARAMETERS--FIXATION PIT

Length of pit	610 cm (20 ft)
Width of pit	305 cm (10 ft)
Depth of pit	305 cm (10 ft)
Duration of fixation operation	7,200 s (2 h)
Windspeed	447 cm/s (10 mi/h)
Wind direction	Along length of pit
Temperature	25 °C
Waste liquid	Two-phase aqueous/organic
Liquid composition	20% chloroform, 20% low-volatility organic, 60% water (by weight)
Chloroform properties	
Molecular weight	119.4 g/g mol
Vapor pressure (25 °C)	208 mm Hg
Diffusivity in air (25 °C)	0.104 cm^2/s
Low-volatility organic properties	
Molecular weight	147 g/g mol

For this waste liquid, Raoult's law applies (Equation (6-18)):

$$y_i^* = X_i P_i^*/P_o$$

$$y_i^* = (0.55)(208 \text{ mm Hg})/760 \text{ mm Hg}$$

$$y_i^* = 0.151 \quad .$$

c. Determine the value of the Fick's law correction factor, F_v:

F_v can be obtained from Table 6-3 by linear interpolation, using the value of $y_i^* = 0.151$. Hence,

$$F_v = 0.889 \quad .$$

d. Estimate the instantaneous emission rate, E_i (g/s) (Equation (6-21)):

$$E_i = \frac{2P_o MW_i y_i^* w}{RT} \sqrt{\frac{D_i 1U}{\pi F_v}}$$

$$E_i = \frac{2(760 \text{ mm Hg})(119.4 \text{ g/g mol})(0.151)(305 \text{ cm})}{(62{,}300 \text{ mm Hg}\cdot\text{cm}^3/\text{g mol}\cdot\text{K})(298 \text{ K})}$$

$$\times \sqrt{\frac{(0.104 \text{ cm}^2/\text{s})(610 \text{ cm})(447 \text{ cm/s})}{(3.14)(0.889)}}$$

$$E_i = 45.4 \text{ g/s.}$$

e. Estimate emissions of chloroform during a 2-h fixation operation:

$$E_{i,T} = \frac{45.4 \text{ g}}{\text{s}} \times \frac{3600 \text{ s}}{\text{h}} \times 2 \text{ h}$$

$$E_{i,T} = \frac{3.27 \times 10^5}{\text{batch}} = \frac{0.327 \text{ Mg}}{\text{batch}} \quad .$$

6.4 OPEN LANDFILLS AND WASTEPILES

6.4.1 Emission Model Equations

The RTI land treatment model (also known as the Allen model,[34] discussed in Section 5.2) is used to estimate the air emission rate of the constituent of interest from open (active) landfills and wastepiles. This model is based on the theory of diffusion out of an infinite flat slab and was intended originally for use in estimating emissions from land treatment operations. The intent of this section is to discuss use of the model with regard to the estimation of emissions from open landfills and wastepiles; a detailed description of the model relevant to land treatment operations and the theoretical basis for the model are presented in Section 5.0 of this report and will not be repeated here.

A land-treatment-type model was selected for estimating emissions from open landfills and wastepiles because (1) no adequate models exist for these sources, and (2) there are a number of similarities in physical characteristics of open landfills, wastepiles, and land treatment operations. A previous EPA study[35] dedicated to the evaluation of models for estimating emissions from hazardous waste TSDF identified only one model for open waste dumps such as landfills and wastepiles--the open dump model. A serious limitation of the model for this application, however, is that it does not account for depletion of the volatilizing chemical from the waste surface. Hence, the open dump model is judged unsuitable for the estimation of emissions from landfills and wastepiles over the time period of interest (months or longer).

The similarity in physical characteristics among open landfills, wastepiles, and land treatment operations is apparent upon close examination--in all three, the waste liquid is ultimately mixed homogeneously with a "carrier" matrix (soil in the case of land treatment; dry fixative in the case of active landfills; and soil, fixative, or some other solid matrix in the case of wastepiles). In all cases, the matrix is porous and permeable, allowing the diffusion of the constituent of interest through the matrix and into the air. Hence, in all cases, diffusion theory can be used to model the emission rate. The notable difference between land treatment operations and open landfills/wastepiles is the presence of an additional mechanism affecting emissions in the case of land treatment--biological decay of the constituent. Because biodegradation is not thought to occur* in open landfills/wastepiles, however, its effect is not accounted for in the modeling of air emissions.

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*There is no evidence that there is significant biomass (necessary for biological decay) in any chemical waste landfill. It is assumed that the toxic property of the waste will inhibit biological processes.[36]

The RTI land treatment model, which was selected for estimating emissions from open landfills and wastepiles, has the following characteristics: a sound basis in scientific theory, limited validation against measured emissions from land treatment operations, and reasonably available input data.[37] The model considers effects such as evaporation of the constituent of interest from interstitial surfaces of the carrier matrix and diffusion of material through air-filled pore spaces.

The equations necessary to apply the land treatment model to open landfills and wastepiles are summarized in Table 6-6. These equations, extracted from Section 5.0, can be used to estimate the fraction of the constituent emitted (F_t) and the instantaneous emission rate (E). It should be noted that the absence of biodegradation represents a special case that allows some simplification of several of the Section 5.0 equations, e.g., Equations (5-4) and (5-5). (The absence of biomass implies that biomass concentration equals 0. Hence, t_b, the time constant for biological decay, equals infinity. Consequently, the exponential term e^{-t/t_b} becomes unity.) Also, the absence of biodegradation implies that the fraction of the constituent emitted after a long time, F_a, would equal unity.

Because the land treatment model was derived originally for land treatment operations, model input parameters are not necessarily in the most convenient units and terminology for open landfills and wastepiles. Hence, several points should be noted:

- Fixed waste is analogous (for modeling purposes) to the waste-laden soil in land treatment.
- M_o, the area-loading of the constituent in g/cm^2, is geared toward land treatment operations. For open landfills and wastepiles, it should be computed as indicated in Table 6-6.
- No "tilling" (as discussed in Section 5.0) is performed in open landfills or wastepiles.

- Waste liquid is "applied" or mixed with fixative only once. Hence, waste "reapplication" (used in the sense discussed in Section 5.0) does not occur in open landfills and wastepiles.

- The waste bed depth in open landfills and wastepiles is analogous to the "depth to which waste is mixed" in land treatment, as discussed in Section 5.0.

The approach required to estimate emissions from open landfills or wastepiles is as follows, based on equations in Table 6-6:

1. Compute the loading of waste liquid (L) in the fixative or soil, using the known waste composition. (For two-phase aqueous organics or organic liquid wastes, L should be computed as grams organic phase per cubic centimeter solid material. For dilute aqueous waste liquids, L equals grams aqueous liquid per cubic centimeter solid material.)

2. Compute the effective diffusion coefficient (D_e).

3. Compute the partition coefficient (Keq).

4. Use the appropriate emission equation to compute the fraction of constituent emitted (F_t) and/or the instantaneous emission rate (E). For wastepile calculations, the time input to these equations should be no greater than the life of the wastepile (retention time).

The sensitivity of the land treatment model to some parameters differs in its application to open landfills and wastepiles from that in land treatment operations because of the difference (in some cases) in the expected range of the parameters. In general, it can be stated that, for application to open landfills and wastepiles, the model is sensitive to the air porosity of the solid waste, the liquid loading in the solid waste, the waste depth, the concentration of the constituent in the waste, and the volatility of the constituent under consideration. In contrast, the model exhibits a relatively low sensitivity to the diffusion coefficient of the constituent in air.

The following major assumptions are associated with the RTI land treatment model and its application to open landfills and wastepiles:

- The waste liquid is mixed uniformly with the carrier matrix (either fixative, soil, or some other granular solid material) before placement in an open landfill or wastepile.

TABLE 6-6. RTI LAND TREATMENT MODEL APPLIED TO OPEN LANDFILLS AND WASTEPILES (NO BIODEGRADATION)

Emission fraction[a]

$$F_{at} = 0.72\,(K_d t)^{1/2} \quad \text{for } \frac{Keq\ D_e t}{l^2} < 0.25 \text{ (valid for no biodegradation only)}$$

$$F_{at} = \frac{8}{\pi^2}\left[\,1 - \exp\,(-K_d t)\,\right] + 0.1878 \text{ (for } \frac{Keq\ D_e t}{l^2} \geq 0.25 \text{ - no biodegradation)}$$

$F_a = 1$ $(t \rightarrow \infty$ - no biodegradation).

$$K_d = \frac{Keq\ \ D_e \pi^2}{4l^2}$$

$$D_e = D_a\,\epsilon_a^{3.33}/\epsilon_T^{2} \qquad \left[D_e/D_a = \epsilon_a^{3.33}/\epsilon_T^{2}\right]$$

$$Keq = \frac{H_c\ (10^6 cm^3/m^3)}{RT} \times \frac{\epsilon_a}{\epsilon_{waste}} \quad \text{(for aqueous waste)}$$

$$Keq = \frac{P^* MW_{oil}}{RT}\,\frac{\epsilon_a}{L} \text{ (for two-phase aqueous/organic or organic liquid waste)}$$

Emission rate

$$E = \frac{2\ M_o\ \ Keq\ D_e}{l^2}\left[\ \exp\ (-\tau)\ \right] \text{ for } Keq\ D_e t/l^2 \geq 0.213$$

$$E = \frac{Mo}{l}\left[\frac{1}{\dfrac{\epsilon_a}{k_G\ Keq} + \left(\dfrac{\pi\ t}{keq\ D_e}\right)^{1/2}}\right] \quad \text{(for all other times)}$$

$$\tau = \frac{D_e Keq\ \pi^2 t}{4l^2}$$

$M_o = l\ L\ C$

$d_e = (4A/\pi)^{1/2}$

$k_G = 4.82\ (10^{-3})\ U^{0.78}\ Sc_G^{-0.67}\ de^{-0.11}$

See notes at end of table.

(continued)

TABLE 6-6 (continued)

Variable	Definition	Data source
C	Weight fraction of constituent in the oil (organic) phase (for two-phase or organic liquid waste), or weight fraction of constituent in the water (for aqueous waste)	Definition
D_a	Diffusion coefficient of constituent in air, cm^2/s	Data base
D_e	Effective diffusion coefficient of constituent in the solid waste, cm^2/s	Calculated
E	Emission rate of constituent, $g/cm^2/s$	Calculated
F_a	Fraction of constituent emitted to the atmosphere at infinity (equals unity for no biodegradation)	Definition
F_t	Fraction of constituent emitted to the atmosphere after time t	Calculated
H_c	Henry's law constant for constituent, $atm \cdot m^3/g$ mol	Data base
K_d	Volatilization constant for constituent, s^{-1}	Calculated
k_G	Gas-phase mass transfer coefficient, m/s	Calculated
Keq	Ratio of gas-phase constituent to total constituent in the solid waste	Calculated
l	Depth of waste in open landfill or wastepile, cm	Literature
L	Waste loading in fixative or soil. For two-phase aqueous/organics or organic liquids, L = g organic (oil) phase/cm^3 solid material. For dilute aqueous waste liquids, L = g aqueous liquid/cm^3 solid material	Definition
A	Area of open landfill, m^2	Definition
M_o	Area loading of constituent, g/cm^2	Calculated

See notes at end of table.

(continued)

TABLE 6-6 (continued)

Variable	Definition	Data source
MW_{oil}	Average molecular weight of the oil (less constituent), g/g mol	Estimated
p^*	Pure component vapor pressure of constituent, atm	Data base
R	Ideal gas constant, 82.05 atm•cm^3/g mol•K	Literature
T	Temperature of vapor in solid waste, K	Assumed
U	Windspeed (m/s)	Assumed
t	Time variable for emission calculation, s (represents time lapse from initial waste composition)	Definition
τ	Dimensionless parameter used in the instantaneous emission rate expression	Calculated
ϵ_a	Void fraction (air porosity) of solid waste (dimensionless)	Estimated from fixed waste property data
d_e	Effective diameter of land treatment area, m	Calculated
Sc_G	Schmidt number	Calculated
ϵ_T	Total porosity of solid waste (dimensionless)	Industry personnel
ϵ_{waste}	Volume fraction of waste liquid in solid waste (dimensionless) (can be computed as L/[density aqueous liquid in g/cm^3])	Calculated

[a] The first equation presented represents a special case of Equation (5-7) for no biodegradation.

[b] This equation represents the first term of the series in Equation (5-5), for the special case of no biodegradation. The exponential terms are expressed, for convenience, in terms of the dimensionless parameter "τ".

- The liquid waste containing the constituent of interest is assumed to be bound in the waste after fixation and placement in the open landfill or wastepile.

- The waste liquid does not flow within the carrier matrix.

- The adsorption isotherm of the constituent of interest is linear within the depth of the waste and does not change with time.

- No bulk flow of gas is induced within the waste matrix.

- The diffusion coefficient does not vary with either concentration or time.

- The concentration of the constituent of interest in the gas phase at the surface of the open landfill/wastepile is much lower than the concentration of the constituent of interest in the gas phase within the waste matrix.

- No diffusion of the waste liquid into depths below the waste layer is assumed.

- Liquid-vapor equilibrium is established at all times within the waste matrix.

- For the case of fixed waste in the landfill or wastepile, the fixed waste mixture behaves as a soil with regard to diffusion of the constituent of interest.

- No biodegradation of the constituent of interest occurs in open landfills or wastepiles.

6.4.2 Model Plant Parameters for Open Landfills and Wastepiles

The characteristics of model facilities for open landfills and wastepiles are discussed here. The model open landfill facility is used as the basis for an example calculation using the model.

6.4.2.1 Parameters for Open Landfills. The model facility for open landfills has a surface area of 1.42×10^8 cm^2 (3.5 acres). This value represents an approximately midrange value from the Westat survey.[38] A reasonable value of landfill depth from the Westat survey[39] was 458 cm (15 ft). The model open landfill is assumed to be half full, and hence has a waste depth of 229 cm (7.5 ft). The landfill is assumed to contain fixed waste. A standard temperature of 25 °C is assumed to apply.

The waste liquid (before fixation) selected for this model facility is assumed to be a two-phase aqueous/organic containing 20 percent chloroform, 20 percent low-volatility organic, and 60 percent water (by weight). This liquid has an average density of 1.16 g/cm^3. The fixation industry indicates that waste liquid, when combined with fixative, may increase in volume by up to 50 percent,[40] depending on the specific combination of waste and fixative. In view of the inherent variability in the fixation process and the lack of real data on volume changes, for purposes of this report, the assumption is made that the waste volume does not change during fixation. Measurements[41] performed on various types of fixed waste yielded a broad range of total porosities. Fifty percent,* as used in this study, is a reasonable estimate of this parameter. A 25-percent* air porosity appears to be a reasonable value; this value was inferred from measurements of total porosity and moisture content.[42] As discussed previously, there is no evidence of significant biomass in any chemical waste landfill. Therefore, in this analysis it is assumed, as suggested in the literature, that the toxic property of the waste will inhibit biological processes and thus prevent biogas generation.[43] Hence, the waste biomass concentration is taken to be 0 g/cm^3.

The properties of chloroform that are pertinent to this analysis include the molecular weight (119.4 g/g mol), pure component vapor pressure (208 mm Hg), and diffusivity in air (0.104 cm^2/s). The low-volatility organic liquid present in the waste has a molecular weight of 147 g/g mol.

Table 6-7 summarizes the model facility parameters for open landfills used in the example calculation in Section 6.4.3.

6.4.2.2 Parameters for Wastepiles. A review of information in the Westat survey[44] led to the selection of an approximately midrange value for basal area of 4.65 x 10^6 cm^2. For modeling purposes, the pile is assumed to be flat. A uniform height of 100 cm was inferred, using the Westat information and engineering judgment. All waste ultimately disposed of in the landfill is assumed to be stored initially in the wastepile. The open landfill described previously (Section 6.4.2.1) is assumed to be filled to capacity in 1 yr. Based on the filled landfill volume (1.42 x 10^8 cm^2 x 458 cm depth = 6.50 x 10^{10} cm^3), the wastepile volume (4.65 x 10^6 cm^2 x

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*These porosity values are assumed to be representative of waste in an open landfill, rather than waste that has recently undergone fixation.

TABLE 6-7. INPUT PARAMETERS--OPEN LANDFILL

Area	1.42×10^8 cm^2 (3.5 acres)
Waste depth	229 cm (7.5 ft)[a]
Volume	3.25×10^{10} cm^3
Temperature	25°C
Waste liquid (before fixation)	Two-phase aqueous/organic
Liquid composition	20% chloroform, 20% low-volatility organic, 60% water (by weight)
Liquid density (average)	1.16 g/cm^3
Liquid/fixative	1 unit volume liquid + dry fixative = 1 unit volume fixed waste
Air porosity fixed waste	0.25 (25%)
Total porosity fixed waste	0.50 (50%)
Biomass concentration	0 g/cm^3
Chloroform properties	
Molecular weight	119.4 g/g mol
Vapor pressure	208 mm Hg
Diffusivity in air	0.104 cm^2/s
Low-volatility organic properties	
Molecular weight	147 g/g mol

[a] Represents half full.

100 cm = 4.65 x 10^8 cm^3), and the filling time of 1 yr, it can be concluded that the wastepile undergoes a turnover rate of 140 turnovers/yr. Hence, the wastepile retention time is 2.6 d/turnover. The properties of the waste liquid and the resulting fixed waste accommodated by the model wastepile are identical to those for the open landfill (Section 6.4.2.1) and will not be repeated here. Table 6-8 summarizes the model facility parameters used for wastepiles.

6.4.3 Example Calculation for Open Landfill

This section presents a step-by-step calculation of emissions from an open landfill. The equations identified in Table 6-6 are used with the model unit parameters in Section 6.4.2 to estimate emissions from a fixed, two-phase aqueous/organic waste containing chloroform; the same equations would be applied to the estimation of emissions from wastepiles:

- Waste liquid (before fixation): 20 percent chloroform, 20 percent low-volatility organic liquid, 60 percent water
- Liquid/fixative: 1 unit volume liquid + dry fixative = 1 unit volume fixed waste
- Waste biomass concentration: 0 g/cm^3
- Landfill area: 1.42 x 10^8 cm^2 (3.5 acres)
- Landfill depth: 229 cm (7.5 ft)
- Temperature: 25 °C
- Time period for emission calculation: 3.15 x 10^7 s (1 yr).

a. Compute waste loading, L:

Liquid density before fixation = 1.16 g/cm^3

1 cm^3 liquid waste + fixative = 1 cm^3 fixed waste

L = g organic phase/cm^3 fixed waste

$= (0.20 + 0.20) \times 1.16 \text{ g/cm}^3 = 0.46 \text{ g/cm}^3$.

(Note that weight fraction of chloroform in the oil phase [C] = 0.2/(0.2 + 0.2) = 0.50.)

TABLE 6-8. INPUT PARAMETERS--WASTEPILES

Surface area	4.65 x 10^6 cm^2
Average height	100 cm
Turnover rate	139/yr
Retention time	2.6 d
Temperature	25 °C
Windspeed	4.92 m/s
Waste type	Fixed waste
Waste liquid (before fixation)	Two-phase aqueous/organic
Liquid composition	20% chloroform, 20% low-volatility organic, 60% water (by weight)
Liquid density (average)	1.16 g/cm^3
Liquid/fixative	1 unit volume liquid + dry fixative = 1 unit volume fixed waste
Air porosity fixed waste	0.25 (25%)
Total porosity fixed waste	0.50 (50%)
Biomass concentration	0 g/cm^3
Chloroform properties	
Molecular weight	119.4 g/g mol
Vapor pressure (25 °C)	208 mm Hg
Diffusivity in air (25 °C)	0.104 cm^2/s
Low-volatility organic properties	
Molecular weight	147 g/g mol

b. Compute effective diffusion coefficient for fixed waste:

$$D_e = D_a \frac{\epsilon_a^{3.33}}{\epsilon_T^{2}}$$

where

ϵ_a = air porosity fixed waste = 0.25

ϵ_T = total porosity fixed waste = 0.50.

Then

D_a = diffusivity of chloroform in air = 0.104 cm^2/s

$$D_e = (0.104\ cm^2/s)\ \frac{(0.25)^{3.33}}{(0.50)^2}$$

$D_e = 4.11 \times 10^{-3}\ cm^2/s$. (Note: $D_e/D_a = 3.96 \times 10^{-2}$.)

c. Compute "partition" coefficient, Keq (ratio of gas-phase chloroform to total chloroform in the waste):

For oily waste,

$$Keq = \frac{P^{*} MW_{oil}}{R\ T}\ \frac{\epsilon_a}{L}$$

where

P^{*} = pure component vapor pressure of chloroform = (208 mm Hg)/(760 mm Hg/atm) = 0.274 atm

MW_{oil} = molecular weight low-volatility organic = 147 g/g mol

R = ideal gas constant = 82.05 cm^3•atm/g mol•K

T = temperature within solid waste, K

T = 273 K + 25 °C = 298 K

$$Keq = \frac{(0.274\ atm)(147\ g/g\ mol)(0.25)}{(82.05\ cm^3 \cdot atm/g\ mol \cdot K)(298\ K)(0.46\ g/cm^3)}$$

$Keq = 8.95 \times 10^{-4}$.

d. Compute fraction of total chloroform emitted, F_t, after 1 year:

First, determine which solution applies by computing $\frac{Keq\ D_e t}{l^2}$ (Table 6-6):

$$\frac{Keq_i D_e}{l^2} = \frac{8.95 \times 10^{-4} \times 4.11 \times 10^{-3}\ cm^2/s}{(229\ cm)^2}$$

$$= 7.01 \times 10^{-11}\ s^{-1}\ .$$

Therefore,

$$\frac{Keq\ D_e t}{l^2} = 7.01 \times 10^{-11}\ s^{-1} \times 3.15 \times 10^{7}\ s$$

$$= 2.21 \times 10^{-3}\ .$$

$$K_d t = \frac{Keq\ D_e t}{l^2}\ \frac{\pi^2}{4} = 5.45\ (10^{-3})\ .$$

Because $Keq\ D_e t/l^2$ is less than 0.25, the first equation of Table 6-6 applies, and

$$F_t = 0.72\ (K_d t)^{1/2}$$

$$F_t = 0.72\ (5.45 \times 10^{-3})^{1/2}$$

$$F_t = 0.053\ .$$

e. Compute instantaneous emission rate, E, after 1 yr:

1. Compute initial mass of chloroform in landfill:

$$M_{oi} = l\ L\ C$$

where

l = waste depth = 229 cm

L = g organic/cm^3 fixed waste = 0.46 g/cm^3

C = weight fraction chloroform in oil = 0.50.

Then

$$M_o = (229 \text{ cm})(0.46 \text{ g/cm}^3)(0.50)$$

$$M_o = 52.7 \text{ g/cm}^2 \quad .$$

3. Compute instantaneous emission rate, E_i. Because Keq $D_e t/l^2 <$ 0.213, use the following equation to compute the emission rate:

$$E = \frac{Mo}{l}\left[\frac{1}{\frac{\epsilon_a}{k_G\ Keq} + \sqrt{\frac{\pi t}{Keq\ D_e}}}\right]$$

$$k_G = 4.82\ (10^{-3})\ U^{0.78}\ Sc_G^{-0.67}\ de^{-0.11}$$

U = windspeed = 4.92 m/s

de = effective diameter of landfill area = $\left(\frac{4A}{\pi}\right)^{0.5}$ = 134 m

$$Sc_G = \frac{\mu g}{\rho_a D_a}$$

where: μg = viscosity of air = 1.8 (10^{-4}) g/cm/s.
ρ_a = Density of air = 1.2 (10^{-3}) g/cm^3.
D_a = 0.104 cm^2/s.

$$Sc_G = \frac{1.81\ (10^{-4})}{1.2\ (10^{-3})\ (0.104)} = 1.45$$

$$k_G = 4.82\ (10^{-3})\ (4.92)^{0.78}\ (1.45)^{-0.67}\ (134)^{-0.11}$$

$$= 0.0076 \text{ m/s} = 0.76 \text{ cm/s}$$

$$E = \frac{52.7}{229}\left[\frac{1}{\frac{0.25}{0.76 \times 8.95(10^{-4})} + \sqrt{\frac{3.14 \times 3.15(10^7)}{8.95(10^{-4}) \times 4.11(10^{-3})}}}\right] = 0.230\left[\frac{1}{368 + 5.18(10^6)}\right]$$

$$E = 4.43\ (10^{-8})\ \text{g/cm}^2\text{/s.}$$

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7.0 TRANSFER, STORAGE, AND HANDLING OPERATIONS

7.1 NARRATIVE DESCRIPTION OF MODEL PLANTS AND EMISSIONS

This section presents models for estimating VO emissions of hazardous wastes from container loading, storage, and cleaning; stationary tank loading and storage; spills; fugitive sources; and vacuum truck loading.

7.2 CONTAINER LOADING

This section addresses emission-estimating practices for hazardous waste loading into tank trucks, railroad tank cars, marine vessels, and 55-gal (0.208-m^3) drums.

7.2.1 Emission Model for Container Loading

The process of loading containers with volatile hazardous wastes generates emissions. If containers were assumed to be clean when loaded, only those vapors generated by the loaded waste could be emitted. If containers hold residues of previous volatile wastes, additional emissions from the residues will also be generated.

To calculate container loading losses, the AP-42[1] equation for loading petroleum liquids is applied. This equation was derived for tanks, cars, and marine vessels. It is also applied to 55-gal drums in this case because the loading principles are similar and because no equation has been developed exclusively for small containers such as drums. The loading equation is as follows:

$$L_L = \frac{12.46\ SMP^*}{T} , \qquad (7\text{-}1)$$

where

L_L = loading loss, lb/10^3 gal of liquid loaded

M = molecular weight of vapors, lb/lb mol

P^* = true vapor pressure of liquid loaded, psia

T = bulk temperature of liquid loaded, °R (°F + 460).

S = saturation factor, dimensionless (see Table 7-1).

Equation (7-1) for estimating emissions from containers is not applicable to open dumpsters because they are designed with no tops, unlike drums that have limited venting through bungs.

7.2.2 Model Parameters

Containers are considered to be splash-loaded (as opposed to submerged-loaded) for emission-estimating purposes. This loading method creates larger quantities of VO vapors and increases the saturation factor, S, of each volatile compound within the container. A saturation factor is a dimensionless quantity that "represents the expelled vapors' fractional approach to saturation and accounts for the variations observed in emission rates from the different unloading and loading methods."[2] A saturation factor of 1.45 was selected for these emission estimates, based on previous documentation of splash-loading petroleum liquids.[3,4]

Typical capacities for containers are assumed to be as follows:

- Drums: 55 gal (0.208 m^3)
- Tank trucks: 7,000 gal (26.5 m^3)
- Railroad tank cars: 30,000 gal (114 m^3)
- Marine vessels: 20,000 tons.

It is assumed that 55-gal drums and tank trucks are the predominant containers used in the waste management industry. Bulk liquid hazardous waste is shipped predominantly by highway; therefore, hazardous waste tank truck models are used for estimating emissions.

Molecular weight and vapor pressure are functions of the waste loaded, and 25 °C is considered an annual average ambient operating temperature.

7.2.3 Sample Calculation for Tank Loading

The following sample calculation may be used to estimate VO emissions from tank truck loading of an organic liquid. Waste stream compounds and properties for the sample calculation are as follows. The same waste stream is employed in each sample calculation in this section; only the type of emission source is varied.

TABLE 7-1. S FACTORS FOR CALCULATING PETROLEUM LOADING LOSSES

Cargo carrier	Mode of operation	S factor
Tank trucks and tank cars	Submerged loading of a clean cargo tank	0.50
	Splash loading of a clean cargo tank	1.45
	Submerged loading: normal dedicated service	0.60
	Splash loading: normal dedicated service	1.45
	Submerged loading: dedicated vapor balance service	1.00
	Splash loading: dedicated vapor balance service	1.00
Marine vessels[a]	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

[a] To be used for products other than gasoline.

Constituent	Weight fraction	Molecular weight (lb/mol)	Vapor pressure (psia)	Mole fraction
Benzene	0.3	78	1.84	0.368
Naphthalene	0.3	128	0.0044	0.224
Phenol	0.4	94	0.0066	0.408

The input parameters for the truck loading model are as follows:

- True vapor pressure of loading liquid, psia: 0.68 (calculated in a., below)
- Molecular weight of vapor, lb/mol: 78.23 (calculated in b., below)
- Saturation factor, dimensionless: 1.45 (splash loading)
- Bulk temperature of liquid loaded, °R: 537
- Annual throughput, gal/yr: 28,000

a. Calculate P^*, true vapor pressure of liquid, by Raoult's Law:

$$P^* = (P_1 \bullet X_1) + (P_2 \bullet X_2) + (P_3 \bullet X_3)$$

where

P^* = true vapor pressure, psia

P_1, P_2, and P_3 = vapor pressures of pure components

X_1, X_2, and X_3 = mole fractions of VO components in liquid

P^* = (1.84 psia x 0.368) + (0.0044 psia x 0.224) + (0.0066 psia x 0.408)

= 0.68 (psia).

b. Calculate M, molecular weight of vapors:

$$M = \frac{(P_1 \bullet X_1)}{P^*} \bullet M_1 + \frac{(P_2 \bullet X_2)}{P^*} \bullet M_2 + \frac{(P_3 \bullet X_3)}{P^*} \bullet M_3$$

where

M = molecular weight of vapor

M_1, M_2, and M_3 = molecular weight of each component

$$M = \left(\frac{1.84 \times 0.368}{0.68}\right) \times 78 + \left(\frac{0.0044 \times 0.224}{0.68}\right)$$

$$\times 128 + \left(\frac{0.0066 \times 0.408}{0.68}\right) \times 94$$

$$= 78.23 \text{ (lb/mol)}.$$

c. Calculate emissions from truck loading:

$$L_L = \frac{12.46 \text{ SMP}^*}{T}$$

$$= \frac{12.46 \times 1.45 \times 78.23 \times 0.68}{537\ °R}$$

$$= 1.79 \text{ lb/1,000 gal}$$

$$\text{Annual emissions, } L_L = \frac{1.79 \times 10^{-3} \text{ lb/gal} \times 28{,}000 \text{ gal/yr}}{2{,}205 \text{ lb/Mg}}$$

$$= 0.023 \text{ Mg/yr} \quad .$$

7.3 CONTAINER STORAGE

This section addresses storage emissions from tank trucks, railroad tank cars, 55-gal drums, marine vessels, and open dumpsters.

7.3.1 Emission Model for 55-Gal Drums, Tank Trucks, and Railroad Tank Cars

With regard to 55-gal drums, container storage is considered a location where multiple drums are most likely to accumulate and be stored for more than 90 days. Because drums are designed to be stored with a sealed lid and bung, the potential for breathing losses is minimal. Therefore, breathing loss is assumed to be negligible. However, the potential does exist for a drum to rupture or become damaged and leak during storage. Thus, the emissions from drum storage may be estimated using the same spill fraction used for drum handling--10^{-4} (to be discussed in more detail in Section 7.7, Spills). The following equation is used to estimate emissions from drum storage:[5]

$$E = 10^{-4} \times I \times W_i \times V_i \qquad (7\text{-}2)$$

where

E = emission from drum storage, Mg/yr

I = throughput, Mg/yr

W_i = VO weight fraction

V_i = volatilization fraction.

Emission-estimating methodologies have not been developed for storage in tank trucks and railroad tank cars. Only loading information was available in the literature for these containers. The assumed same emission estimates principle for drum storage is applied with an emission factor of 10^{-5} (to be discussed in more detail in Section 7.7, Spills).[6]

7.3.2 Model Parameters for Drum Storage

It is assumed that 50 percent of the VO storage loss from drum spill or rupture will be volatilized. The remaining volatiles will be captured with RCRA spill response measures taken at the facility.

7.3.3 Sample Calculations for Drum Storage

Input parameters:

Waste stream: organic liquid
(See Section 7.2.3 for constituents.)
Waste density: 1.04 Mg/m^3
Drum storage capacity: 182 drums (0.208 m^3/drum)
Turnovers per year: 12
Spill fraction: 10^{-4}
Weight fraction: 1
Volatilization fraction: 0.5.

a. Calculate annual throughput, I, Mg/yr:

$$I = 182 \times 0.208\ m^3 \times 12 \times 1.04\ Mg/m^3$$

$$= 472\ Mg/yr\ .$$

b. Calculate air emissions:

$$E = 10^{-4} \times I \times W_i \times V_i$$

$$= 10^{-4} \times 472 \text{ Mg/yr} \times 1 \times 0.5$$

$$= 0.024 \text{ Mg/yr} \quad .$$

7.3.4 Emission Model for Open Dumpsters

No information was found in readily available literature to estimate VO emissions from the storage of hazardous wastes in open-top dumpsters. The wastes held in dumpsters may range from sludges to contaminated filters. An emission algorithm[7,8] was developed for losses from an open dump. Because an open dumpster is similar to an open dump, this algorithm was used to calculate storage emissions. (See Section 6.3 for a detailed derivation of the open dump model.)

$$E_i = \frac{2 \, P_o \, MW_i \, Y_i^* \, w}{RT} \sqrt{\frac{D_i \, l \, U}{\pi \, F_v}} \quad . \tag{7-3}$$

The open dump model is valid for short-term emission estimates only. For long-term emission estimates, to avoid overestimates, it is important to subtract the emissions from the waste's VO content on a daily, weekly, or monthly basis depending on the waste volatility; this is done to identify the point in time when no VO remain in the waste.

7.3.5 Model Parameters for Open Dumpster Storage

The input parameters required for the model are divided into three groups:

- Meteorological conditions. An average annual ambient temperature of 25 °F and an average windspeed of 447 cm/s were used.

- Size of the dumpster. A 4-yd^3 uncovered dumpster with the following dimensions was used:

  Length = 1.85 m (73 in)
  Width = 1.45 m (57 in)
  Height = 1.22 m (48 in)

- Properties of waste stored. These properties include molecular weight, vapor pressure, and diffusivity in air. The properties of specific compounds were obtained from literature sources.

7.3.6 Sample Calculation for Open Dumpster Storage

Input parameters:

Waste stream: organic liquid (see Section 7.2.3 for constituents)

VO constituent = benzene

Initial VO amount, Mg = 2.36

P^*, pure compound vapor pressure, mm Hg = 95.2

P_o, atmospheric pressure, mm Hg = 760

U, windspeed, cm/s = 447

l, length of the dumpster, cm = 185.42

w, width of the dumpster, cm = 144.78

D_i, diffusion coefficient of VO in air = 0.088

X_i, mole fraction of VO in liquid = 0.368

Y_i^*, mole fraction of VO in gas phase = 0.046 (calculated in a., below)

MW_i, molecular weight = 78

T, ambient temperature, K = 298

R, gas constant, $\frac{\text{mm Hg cm}^3}{\text{g mol} \cdot \text{K}}$ = 62,300

F_v, correction factor for Fick's law = 1.0 (calculated in b., below)

N, dumpster turnovers per year = 2

a. Calculate the equilibrium mole fraction of VO in the gas phase Y_i^*:

$$Y_i^* = (X_i)(P^*)/P_o$$

$$= \frac{0.368 \times 95.2 \text{ mm Hg}}{760 \text{ mm Hg}}$$

$$= 0.046 \quad .$$

b. Determine the value of the Fick's law correction factor, F_v. F_v can be obtained from Table 6-3 by linear interpolation, using the value of $Y_i^* = 0.046$. Hence, $F_v = 1.0$.

c. Estimate the short-term emission rate for benzene, E_i (g/s):

$$E_i = \frac{2\ P_o\ MW_i\ Y_i^*\ w}{RT} \sqrt{\frac{D_i lU}{\pi\ F_v}}$$

$$= \frac{2(760)(78)(0.046)(144.78)}{(62{,}300)(298)} \sqrt{\frac{(0.088)(185.42)(447)}{(3.1416)(1.0)}}$$

$$= 2.06 \text{ g/s}$$

$$= 180 \text{ kg/day.}$$

d. Repeat the above procedures, a. through c., to compute emission rate for each constituent as follows:

	Emission rate, g/s	Emissions, kg/d
Benzene	2.06	180
Naphthalene	0.004	0.3
Phenol	0.0093	0.0

e. Estimate annual emissions, Mg/yr:

For high volatile benzene with a 6-mo turnover time, all of the benzene will emit to the atmosphere in the first week.

	Init. VO, Mg	Annual emissions	
		Mg/turnover	Mg/yr
Benzene	0.708	0.708	1.416
Naphthalene	0.708	0.062	0.124
Phenol	0.944	0.145	0.290
Total	2.360	0.915	1.830

7.4 CONTAINER CLEANING

7.4.1 Emission Model for Container Cleaning

An AP-42 document[9] on tank truck cleaning is used as the primary source for container-cleaning emission estimates. AP-42 states that tank truck cleaning typically involves washing the truck interior with agents such as water, steam, detergents, or other chemicals. The document also provides emission factors that are a function of vapor pressure and viscosity. These factors have been applied to emission estimates for cleaning all types of containers, as follows:

Tank truck residue to be removed	Emission factor g/truck (lb/truck)
High vapor pressure, low viscosity	215 (0.474)
Medium vapor pressure, medium viscosity	32.4 (0.071)
Low vapor pressure, low viscosity	5.5 (0.012)

The following equation is used to estimate emissions for container cleaning:

$$E = F_c \times N \times W_i \times 10^{-6} \qquad (7\text{-}3)$$

where

E = cleaning loss, Mg/yr

F_c = emission factor for cleaning, g/container

N = number of cleanings per year

W_i = VO weight fraction.

7.4.2 Model Parameters

In all containers, the primary input parameter for estimating cleaning emissions is the cleaning emission factor, which is determined from (1) residue vapor pressure and viscosity (functions of waste handled), and (2) container volume.

Based on AP-42,[10] a typical tank truck volume of 26.5 m^3 (7,000 gal) is assumed.

Because no data are currently available for drum cleaning, the emission factors for tank trucks were used to calculate cleaning emissions from drums by comparing the proportion of drum volume (55 gal) to that of the tank truck (7,000 gal).

55-Gal drum residue to be removed	Emission factor g/drum	(lb/drum)
High vapor pressure, low viscosity	1.69	(0.0037)
Medium vapor pressure, medium viscosity	0.25	(0.0006)
Low vapor pressure, low viscosity	0.04	(0.00009)

Emissions from marine vessels have not been addressed because of the low usage of such vessels in the waste management industry.

7.4.3 Sample Calculation for Tank Truck Cleaning

The general assumptions for truck cleaning are as follows:

- Residue: pure organic liquid (benzene)
- Number of truck cleanings per year: 4
- Truck capacity: typical truck
- Weight fraction: 1.

a. Determine the cleaning emission factor, F_c:

(215 g/truck was used because of high vapor pressure and low viscosity of pure benzene residue).

b. Calculate cleaning emissions:

$$E = F_c \times N \times W_i \times 10^{-6}$$

$$= 215 \text{ g} \times 4 \times 1 \times 10^{-6} \text{ Mg/g}$$

$$= 8.6 \times 10^{-4} \text{ Mg/yr} \quad .$$

7.5 STATIONARY TANK LOADING

7.5.1 Emission Model for Stationary Tank Model

Stationary tank working losses are those emissions from waste loading and unloading operations. AP-42's "Storage of Organic Liquids"[11] provides an equation to estimate loading and unloading emissions from storage tanks. The equation was developed for handling VO liquid in the following industries:

- Petroleum producing/refining
- Petrochemical and chemical manufacturing
- Bulk storage and transfer operations
- Other industries consuming or producing organic liquids.

Because hazardous wastes have the potential to contain VO compounds, as do organic liquids, and because they are most commonly stored in the same fashion as these liquid products, the following equation was selected from AP-42:

$$L_w = 2.40 \times 10^{-5} M_v \bullet P^* \bullet V \bullet N \bullet K_n \bullet K_c \tag{7-4}$$

where

L_w = working losses, lb/yr

M_v = molecular weight of vapor in storage tank, lb/lb mol

P^* = true vapor pressure at bulk liquid conditions, psia

N = number of turnovers per year (dimensionless)

$N = \frac{\text{total throughput per year (gal)}}{\text{tank capacity, V (gal)}}$

V = tank capacity, gal

K_n = turnover factor, dimensionless (for turnovers ≤ 36, $K_n = 1$; for turnovers > 36, $K_n = \frac{180 + N}{6N}$)

K_c = product factor, dimensionless (for crude oil, $K_c = 0.84$; for all other organic liquids, $K_c = 1$).

7.5.2 Model Parameters

It is assumed that all stationary tanks are fixed-roof. According to responses to the 1982 Westat Mail Survey,[12] which were examined by the GCA Corporation,[13] there are four sizes of tanks that best represent the waste management industry:

- 5.3 m^3 (1,500 gal)
- 30.3 m^3 (8,000 gal)
- 75.0 m^3 (20,000 gal)
- 795 m^3 (210,000 gal).

Table 7-2 lists typical input parameters for these model tanks. Turnovers per year were selected based on volume of waste processed in waste management scenarios recorded in various documents. Molecular weight and vapor pressure are a function of the waste loaded.

7.5.3 Sample Calculation for Tank Loading Emission Model

Input parameters:

Waste stream: organic liquid (see Section 7.2.3 for constituents)
M_v, molecular weight of vapor, lb/lb mol: 78.23
P^*, true vapor pressure of loading liquid, psia: 0.68
K_C, product factor for working loss: 1
V, fixed-roof tank capacity, gal: 20,000
N, turnovers per year: 44
K_n, turnover factor, dimensionless: 0.848.

a. Calculate M_v, molecular weight of vapor:

(see Section 7.2.3 for calculation).

b. Calculate P^*, true vapor pressure of loading liquid:

(see Section 7.2.3 for calculation).

c. Calculate K_n, turnover factor: because $N = 44$, $K_n = \frac{180 + N}{6N} = 0.848$

d. Calculate air emissions:

$$L_w = 2.40 \times 10^{-5} \times M_v \bullet P^* \bullet V \bullet N \bullet K_n \bullet K_C$$
$$= 2.40 \times 10^{-5} \times 78.23 \times 0.68 \times 20{,}000 \times 44 \times 0.848 \times 1$$
$$= 953 \text{ lb/yr}$$
$$= 0.43 \text{ Mg/yr} \; .$$

TABLE 7-2. PERTINENT FIXED-ROOF TANK SPECIFICATIONS[14,15,16]

Specifications	Model A	Model B	Model C	Model D
Capacity, m^3 (gal)	5.3 (1,500)	30.3 (8,000)	75.7 (20,000)	795 (210,000)
Tank height, m	2.4	2.4	2.7	12.2
Tank diameter, m	1.7	4	5.8	9.1
Average vapor space height, m	1.2	1.2	1.4	6.1
Adjustment for small diameter (dimensionless)	0.26	0.65	0.86	1
Average diurnal temp. change, °C (°F)	11 (20)	11 (20)	11 (20)	11 (20)
Paint factor (dimensionless)	1	1	1	1
Relation of tank to ground	Above	Above	Above	Above
Product factor	1	1	1	1

7.6 STATIONARY TANK STORAGE

7.6.1 Model Description

Fixed-roof tank storage of hazardous wastes results in VO "breathing" emissions through vents as ambient temperature and barometric pressure fluctuate. Emissions occur in the absence of any liquid level change in the tank. An existing AP-42[17] equation was used to estimate VO breathing losses from hazardous waste storage tanks as follows:

$$L_b = 2.26 \times 10^{-2} M_v \left[\frac{P^*}{P_A - P^*}\right]^{0.68} \bullet D^{1.73} \bullet H^{0.51} \bullet \Delta T^{0.5} \bullet F_p \bullet C \bullet K_c \tag{7-5}$$

where

L_b = fixed-roof breathing loss, lb/yr

M_v = molecular weight of vapor in tank, lb/lb mol

P^* = true vapor pressure at bulk liquid conditions, psia

P_A = average atmospheric pressure at tank location, psia

D = tank diameter, ft

H = average vapor space height, ft (assumed to be one-half of tank height)

ΔT = average ambient diurnal temperature change, °F (20 °F assumed as a typical value)

F_p = paint factor, dimensionless (see Table 7.3)

C = adjustment factor for small diameter tanks, dimensionless (for diameter $\geq$ 30 ft, $c = 1$; for diameter < 30 ft, $c = 0.0771\ D - 0.0013\ D^2 - 0.1334$)

K_c = product factor, dimensionless (for crude oil, $K_c = 0.65$, for all other organic liquids, $K_c = 1.0$).

7.6.2 Model Parameters

Table 7-3 identifies the model parameters for estimating tank breathing losses. Molecular weight and vapor pressure are functions of the waste stored.

TABLE 7-3. PAINT FACTORS FOR FIXED-ROOF TANKS[18]

Tank color		Paint factors (F_p) Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44[a]
Medium gray	Medium gray	1.40	1.58[a]

[a] Estimated from the ratios of the seven preceding paint factors.

7.6.3 Sample Calculation for Tank Storage Emission Model

Input parameters:

Waste stream, organic liquid (see Section 7.2.3 for constituents)

M_v, molecular weight of vapor, lb/lb mol: 78.23

P^*, true vapor pressure of loading liquid, psia: 0.68

K_C, product factor for breathing loss: 1

v, fixed-roof tank capacity, gal: 20,000

D, tank diameter, ft: 19

H, average vapor space height, ft: 4.5

ΔT, diurnal temperature change, °F: 20

F_p, paint factor, dimensionless: 1

C, adjustment factor for small tanks: 0.86 (calculate in c., below)

a. Calculate molecular weight of vapor:

(see Section 7.2.3 for calculation).

b. Calculate true vapor pressure of loading liquid:

(see Section 7.2.3 for calculation).

c. Calculate adjustment factor for small tanks:

$$C = 0.0771 \times 19 - 0.0013(19)^2 - 0.1334$$

$$= 0.86 \quad .$$

d. Calculate air emissions:

$$L_b = 2.26 \times 10^{-2}\, M_v \left(\frac{P^*}{P_{\bar{A}}P^*}\right)^{0.68} \bullet D^{1.73} \bullet H^{0.51} \bullet \Delta T^{0.5} \bullet F_p \bullet C \bullet K_c$$

$$= 2.26 \times 10^{-2} \times 78.23 \times \left(\frac{0.68}{14.7-0.68}\right)^{0.68} \times (19)^{1.73} \times (4.5)^{0.51}$$

$$\times (20)^{0.5} \times 1 \times 0.86 \times 1$$

$$= 300 \text{ lb/yr}$$

$$= 0.14 \text{ Mg/yr} \quad .$$

7.7 SPILLS

7.7.1 Model Description

An ICF study[19] of truck transport to and from TSDF and truck emissions at TSDF terminals provided the background information necessary to estimate spillage losses during TSDF and trucking operations. As a result of this study, spill fractions of 10^{-4} and 10^{-5} were assumed for drum movement of wastes and all other remaining waste movement, respectively. Thus, for every 10,000 Mg of drummed hazardous waste moved, 1 Mg is assumed to be spilled. The following equation is used to estimate spill emissions:

$$E = F_s \times I \times W_i \times V_i \qquad (7\text{-}6)$$

where

E = spill emissions, Mg/yr

F_s = emission fraction, 10^{-4} or 10^{-5}

I = annual throughput, Mg/yr

W_i = VO weight fraction

V_i = fraction for volatilization.

7.7.2 Model Parameters

In both cases of spills, it is assumed that 50 percent of the volatiles in the waste are lost. The remaining 50 percent are recovered by RCRA spill plan response. Therefore, most spills would be mitigated before 100 percent of VO is lost to the atmosphere.

It is assumed that spills do not occur during the transfer of waste into a stationary tank if loading is automated through fixed piping.

7.7.3 Sample Calculation for Drum Storage Model

Input parameters:

Waste stream: organic liquid (see Section 7.2.3 for constituents)
Waste density: 1.04 Mg/m^3
Emission fraction: 10^{-4}
Weight fraction: 1
Volatilization fraction: 0.5
Number of drums handled: 2,184 (0.208 m^3/drum).

a. Calculate annual throughput, I, Mg/yr:

$I = 2{,}184 \times 0.208\ m^3 \times 1.04\ Mg/m^3$

$= 472\ Mg/yr$.

b. Calculate air emissions:

$E = 10^{-4} \times 472\ Mg/yr \times 1 \times 0.5$

$= 0.024\ Mg/yr$.

7.8 FUGITIVE EMISSIONS

7.8.1 Emission Model for Fugitives

Waste transfer operations often involve pumping wastes through pipelines into a variety of containment units. Such pumping creates the potential for fugitive emission losses from pumps, valves, and flanges. Table 7-4 presents the Synthetic Organic Chemical Manufacturing Industries (SOCMI) emission factors[20] that had been developed to estimate VO that leak from pump seals, valves, and flanges. These factors are independent of the throughput, type, or size of the process unit.

TABLE 7-4. SOCMI EMISSION FACTORS FOR FUGITIVE LOSSES

Equipment	Type of service	Emission factor (kg/h-source)
Pump seals	Light liquid	4.94 E-2
Valves	Light liquid	7.10 E-3
Flanges	--	8.30 E-4

The following equation is used to estimate fugitive emissions:

$$E = \Sigma\ (F_f \times N_i) \times h \times 10^{-3} \qquad (7\text{-}7)$$

where

E = fugitive emissions, Mg/yr

F_f = emission factor per source-type, kg/h-source (see Table 7-4)

N_i = number of sources per source-type

h = residence time in the equipment (assume = 8,760 h/yr).

7.8.2 Model Parameters

The major input parameters required for the emission model are emission factor, number of sources, and residence time. It is assumed that waste remains in the transfer equipment 24 h/d, 365 d/yr; therefore, VO are continuously being leaked to the atmosphere.

Minimal information has been compiled on typical quantities of pumps, valves, and flanges at waste management facilities. Therefore, previous contractors have turned to data collected from the petroleum refining industry and SOCMI. GCA recommended that "for any hazardous waste filling operation, transfer operation, or handling operation involving pumps, the estimate of two pumps, 35 valves, and 80 flanges be used. This includes tank filling, tank truck or car filling, and drum filling."[21] Because the relationship 2:35:80 appears to be too high for pumping waste into a single drum, one pump, three valves, and eight flanges are used for estimating emissions. GCA recommended that smaller quantities of pumps, valves, and flanges identified by SOCMI be applied for transfer operations to injection wells and incinerators, i.e., 1 pump, 18 valves, and 40 flanges.[22]

7.8.3 Sample Calculation for Fugitive Emission Model

Estimate the annual fugitive emissions from a set of piping lines that connect to a storage tank, given the following information.

Input parameters:

Assume 2 pumps, 35 valves, and 80 flanges associated with the piping equipment.

Assume the waste stream is organic liquid.

Assume waste remains in piping line 24 h/d, 365 d/yr.

a. The emission factor for light liquids was used because of the high VO content.

b. Calculate fugitive emissions:

$$E = (0.0494 \text{ kg/h} \times 2 + 0.0071 \text{ kg/h} \times 35 + 8.3 \times 10^{-4} \text{ kg/h} \times 8)$$

$$\times 8{,}760 \text{ h/yr} \times 10^{-3} \text{ Mg/kg} = 3.62 \text{ Mg/yr} \quad .$$

7.9 VACUUM TRUCK LOADING

7.9.1 Emission Model for Vacuum Truck Loading

Emissions from vacuum truck loading are estimated by calculating an equilibrium concentration of organic vapors in the vacuum truck at its operating conditions and assuming that a total volume of gas equal to the vacuum truck volume is emitted to the atmosphere for each loading episode. Equations for making the calculations are presented as follows:

$$E_i = N_v \times Y_i \times MW_i$$

$$Y_i = \frac{X_i \; P^*}{P_t} \quad \text{(for oily waste)}$$

$$N_v = \frac{V}{[P_o \; V_G \; (T/273)]/P_t}$$

where

E_i = air emissions of compound i, g/truckload

N_v = total moles of vapor discharged, g mol

Y_i = mole fraction of compound i in vapor phase

X_i = mole fraction of compound i in liquid phase

MW_i = molecular weight of compound i, g/g mol

P^* = vapor pressure of compound i, mm Hg

P_t = total system operating pressure, mm Hg

P_o = atmospheric pressure, mm Hg

V = vacuum truck volume, m^3

V_G = volume of 1 g mol of gas at STP, 0.0224 m^3/g mol

T = operating temperature, K.

7.9.2 Model Parameters

Based on information obtained during site visits to refineries using land treatment, vacuum trucks have a capacity of about 21 m^3 (5,500 gal) and operate at a pressure of approximately 303 mm Hg. These values are used in estimating vacuum truck emissions.

Molecular weight and vapor pressure are functions of waste loaded, and 25 °C is considered a standard operating temperature.

7.9.3 Sample Calculation

The following is a sample calculation of benzene emissions during loading of a vacuum truck with organic liquid.

Input parameters:

Waste stream: organic liquid (see Section 7.2.3 for constituents)

VO constituent: benzene

MW_i, molecular weight, g/g mol: 78

P^*, pure compound vapor pressure: 95.2

P_t, system operating pressure, mm Hg: 303

P_o, atmospheric pressure, mm Hg: 760

X_i, mole fraction in liquid: 0.368

V, vacuum truck volume, m^3: 21

V_G, volume of 1 g mol of gas at STP, m^3/g mol: 0.0224

T, operating temperature, K: 298

N, turnovers per year, truckload/yr: 10.

a. Calculate total moles of vapor discharged, g mol:

$$N_v = \frac{V}{[P_a\ V_G\ (T/273)]/P_t}$$

$$= \frac{21\ m^3}{(760\ mm\ Hg \times 0.0224\ m^3/g\ mol \times 298\ K/273\ K)/303\ mm\ Hg}$$

$$= 342.41\ g\ mol/truckload\ .$$

b. Calculate mole fraction of benzene in vapor phase, Y_i:

$$Y_i = \frac{P^*\ X_i}{P_t} = \frac{95.2\ \ 0.368}{303} = 0.1156\ .$$

c. Calculate air emissions per truckload, g/truckload:

$$E_i = N_v \times Y_i \times MW_i$$

$$= (342.41\ g\ mol/truckload)\ (0.1156)\ (78\ g/g\ mol)$$

$$= 3{,}087\ g/truckload\ .$$

d. Calculate annual emissions for benzene, Mg/yr:

Annual emission = $E_i \times N$

= 3,087 g/truckload x 10 truckload/yr

= 30,870 g/yr

= 0.031 Mg/yr .

e. Repeat the above procedures, a through d., to compute emissions for each constituent as follows:

Constituent	E_i, g/truckload	Annual emissions, Mg/yr
Benzene	3,087	0.031
Naphthalene	7	0.00007
Phenol	14	0.00014
Total emissions	3,108	0.0312

7.10 REFERENCES

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19. Reference 5.

20. U.S. Environmental Protection Agency. Control of Volatile Organic Compound Leaks from Synthetic Organic Chemical and Polymer Manufacturing Equipment. Research Triangle Park, NC. Publication No. EPA-450/3-83-006. March 1984.

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8.0 COMPARISON OF MODEL RESULTS WITH FIELD TEST DATA

8.1 INTRODUCTION

Predictions from TSDF emission models are compared with field test data in this section. In general, considering the uncertainty of field emission measurements, agreement between measured and predicted values is considered reasonable. Measured and predicted emissions generally agree within an order of magnitude.

The following caveats must be considered in any evaluation of the comparison results presented in the following sections:

1. The field test data did not always include all of the input parameters required to use the emission models. In such cases, parameter values representative of field operations were used as defaults.
2. The emission models use average influent and effluent concentrations to estimate annual emissions. Variations in concentrations and constituents are not reflected.
3. Field test data provide information on a limited number of hazardous constituents. Extrapolation of comparisons on limited constituents to all constituents of interest may not always be possible.
4. The method of measuring emissions (e.g., flux chambers and other enclosure systems) could alter the real-world system being tested and affect the representativeness of the measured emissions.

8.2 SURFACE IMPOUNDMENTS AND OPEN TANKS

8.2.1 Summary

Emission test data were available from tests of five quiescent surface impoundments. The overall mass transfer coefficients determined in these tests agreed generally within an order of magnitude with the overall coefficient predicted by the mass transfer correlations described in

Section 4.0. Predicted values were higher than measured values in some cases and lower in others.

The emission models used for impoundments also were applied to open tanks. The comparison of measured and predicted values for the overall mass transfer coefficient for open wastewater treatment tanks yielded mixed results. For tanks with quiescent surfaces (e.g., clarifiers and equalization basins), the model predictions were generally lower than measured values but agreed within an order of magnitude. For the aerated systems, the model predictions agreed well with material balance and ambient air measurements for an open aerated system.

8.2.2 Details of Comparisons

The approach to the comparison of predicted and measured values is to estimate the overall mass transfer coefficient from the correlations given in Section 4.0 and to compare this value to the overall mass transfer coefficient from the test data. The overall mass transfer coefficient from the test data is calculated from a measured emission rate and a measured or estimated bulk concentration in the liquid phase. Note that errors in either the measured emission rate or liquid-phase concentration have a direct effect on the errors in the calculated mass transfer coefficient.

Most of the measured emission data were obtained by flux chamber measurements. At a few sources, ambient air monitoring and material balances were used to determine the emission rate for calculation of the overall mass transfer coefficient.

GCA Corporation performed an analysis of data from impoundments. The results are given in Tables 8-1 through 8-4 for four ponds at two different sites. Site 5 is a commercial hazardous waste facility with a wastewater treatment system onsite. The reducing lagoon receives wastes classified as reducing agents from tank trucks. The lagoon is operated on a batch basis and was observed to contain a zone of solids and a surface with a floating oil film. The holding pond receives aqueous wastes from the water treatment system and is filled (and discharged) on a monthly basis. The oxidizing lagoon receives oxidizing agents including halogens and other organic compounds. The accumulation of solids and oil film also was observed on this lagoon. Site 4 also is a commercial hazardous waste facility, and its

TABLE 8-1. COMPARISON OF RESULTS FOR REDUCING LAGOON 1 AT SITE 5[1,2]

Constituent	Mass transfer coefficient (x 10^6 m/s) Average flux chamber measurement[a]	 Model predictions (for 5 to 10 m/s windspeed)[b]
Benzene	4.9	4.2-17
Toluene	5.0	3.9-15
Ethylbenzene	5.5	3.6-14
Naphthalene	2.6	3.5-14
Methylene chloride	12	4.7-19
Chloroform	5.7	4.3-17
1,1,1-Trichloroethane	7.6	3.9-15
Carbon tetrachloride	11	3.9-16
p-Dichlorobenzene	2.6	3.6-14
Styrene	5.7	3.7-15

[a] Calculated from reported emission rate and corresponding liquid-phase concentration.

[b] Windspeed during the test ranged from 5 to 10 m/s.

TABLE 8-2. COMPARISON OF RESULTS FOR HOLDING POND 6 AT SITE 5[3,4]

Constituent	Mass transfer coefficient (x 10^6 m/s) Average flux chamber measurement[a]	Model predictions (for 5 to 10 m/s windspeed)[b]
Benzene	2.7	5.3-21
Toluene	2.3	4.9-19
Ethylbenzene	2.6	4.6-18
Naphthalene	1.6	4.4-18
Methylene chloride	3.1	6.0-24
Chloroform	2.2	5.4-21
1,1,1-Trichloroethane	3.9	4.9-19
Chlorobenzene	<0.039	4.9-20
p-Dichlorobenzene	4.3	4.6-18
Acetaldehyde	3.4	5.7-19

[a] Calculated from reported emission rate and corresponding liquid-phase concentration.

[b] Windspeed during the test ranged from 5 to 10 m/s.

TABLE 8-3. COMPARISON OF RESULTS FOR OXIDIZING LAGOON 2 AT SITE 5[5,6]

Constituent	Mass transfer coefficient (x 10^6 m/s) Average flux chamber measurement[a]	Model predictions (for 5 to 10 m/s windspeed)[b]
Toluene	0.38	3.8-15
Ethylbenzene	0.037	3.6-14
1,1,1-Trichloroethane	35	3.9-15

[a] Calculated from reported emission rate and corresponding liquid-phase concentration.

[b] Windspeed during the test ranged from 5 to 10 m/s.

TABLE 8-4. COMPARISON OF RESULTS FOR SURFACE IMPOUNDMENT AT SITE 4[7,8]

	Mass transfer coefficient (x 10^6 m/s)		
	Flux chamber measurement[a]		Model predictions (for 5 to 10 m/s windspeed)[b]
Constituent	Average	Range	
Toluene	2.4	1.9-2.7	6.3-25.1
Ethylbenzene	1.0	0.46-1.4	5.9-23.5
Methylene chloride	8.4	5.6-10.0	7.7-30.5
1,1,1-Trichloroethane	2.6	1.1-3.6	6.3-24.7
Chloroform	12.0	5.4-15.0	7.0-27.6
p-Dichlorobenzene	0.44	0.079-0.75	5.9-23.1

[a] Results for June 22, 1984.

[b] Windspeed during the test ranged from 5 to 10 m/s.

impoundment is used to contain aqueous wastes. Table 8-5 presents a comparison of results for Site 3, which is a chemical manufacturing plant that produces primarily nitrated aromatics and aromatic amines. This impoundment is a wastewater holding pond for the wastewater treatment system at the plant. Two wastewater streams that enter the treatment system are distillation bottoms from aniline production (K083) and the nitrobenzene production wastewater (K104).

The results in Tables 8-1 through 8-5 show a reasonable agreement between measured and predicted values of the overall mass transfer coefficient. The measured results for the impoundment in Table 8-3 may have been affected by an oil film observed on the surface or from poor mixing in the impoundment, which can complicate representative sampling of the liquid-phase concentration. Table 8-5 shows good agreement of results for toluene and benzene, which were present in the liquid phase at 2.6 and 17 mg/L, respectively. The liquid-phase concentrations of the other four compounds in Table 8-5 ranged from 0.029 to 0.15 mg/L. The differences in measured and predicted values for these four compounds may have been affected by the accuracy of sampling and analysis of the liquid. The compounds listed in Tables 8-1 through 8-5 are controlled by the liquid-phase mass transfer. Consequently, the results are most dependent on Springer's correlation for k_L (the liquid-phase mass transfer coefficient) and suggest that Springer's model is probably accurate within an order of magnitude.

GCA, in a separate document, examined measured and predicted mass transfer coefficients for open tanks that are part of wastewater treatment systems.[10] The results for Site 8, which is an industrial wastewater treatment operation, included a primary clarifier, an equalization basin, and aerated stabilization basins. The various influent and effluent liquid streams were analyzed, and air emissions around the unit were monitored. Overall mass transfer coefficients were calculated from material balance data and from ambient air monitoring. These values are listed in Tables 8-6 through 8-8 along with the predicted values from the mass transfer correlations given in Section 4.0. The primary clarifier, equalization basin, and the quiescent portion of the stabilization basin were modeled as quiescent surfaces, and the correlations of Springer and MacKay/Matasugu

TABLE 8-5. COMPARISON OF RESULTS FOR WASTEWATER HOLDING LAGOON AT SITE 3[9]

Constituent	Mass transfer coefficient (x 10^6 m/s) Flux chamber measurement	Predicted[a]
Cyclohexane	0.39	3.8
Tetrachloroethylene	0.10	3.7
Toluene	9.0	3.8
Benzene	3.7	4.1
n-Undecane	0.21	2.8
Methylchloride	35.0	3.1

[a] Based on an average measured windspeed of 3.7 m/s and an average temperature of 22 °C.

TABLE 8-6. COMPARISON OF RESULTS FOR PRIMARY CLARIFIERS AT SITE 8[11]

	Mass transfer coefficient (x 10^6 m/s)		
Constituent	Material balance	Ambient monitors	Model prediction
Tetralin	--	227.0	--
2-Ethyl hexanol	96.0	42.0	2.0
2-Ethyl hexyl acrylate	--	123.0	2.7
Naphthalene	179.0	92.0	3.4
1,2-Dichloroethane	58.0	2.9	4.0
Benzene	5.4	18.0	4.1
Toluene	35.0	50.0	3.8
Ethyl benzene	156.0	39.0	3.5

TABLE 8-7. COMPARISON OF RESULTS FOR EQUALIZATION BASIN AT SITE 8[12]

Constituent	Mass transfer coefficient (x 10^6 m/s) Material balance	Ambient monitors	Model prediction
1,2-Dichloroethane	20	19.0	5.0
Benzene	20	8.9	5.1
Toluene	25	42.0	4.7
Ethyl benzene	25	5.4	4.4

TABLE 8-8. COMPARISON OF RESULTS FOR AERATED STABILIZATION BASINS AT SITE 8[13]

Constituent	Mass transfer coefficient (x 10^4 m/s) Material balance	Ambient monitors	Model prediction
2-Ethyl hexanol	0.05	0.01	0.17
2-Ethyl hexyl acrylate	4.8	8.3	2.9
1,2-Dichloroethane	2.0	0.52	5.7
Benzene	12.4	1.1	10.6
Toluene	5.0	5.8	10.1
Ethyl benzene	2.9	0.55	9.9

were used. The turbulent portion of the stabilization basins was modeled using the correlations of Thibodeaux and Reinhardt.

Useful conclusions from the comparison of measured and predicted values are difficult because of the lack of consistent results from air monitoring, probably due to very short sampling periods, changes in the windspeed and direction, and the contribution to emissions from sources near the mentioned source. In addition, material balance calculations are subject to error from changes in influent/effluent flow rates and concentrations of specific compounds. In general, the model predictions for the primary clarifier and equalization basin are lower than the measured values. For the aerated stabilization basin, most of the predicted mass transfer coefficients are higher than the measured values; however, the agreement is within an order of magnitude. The measured values for the primary clarifier may have been higher than the predicted values because of the contribution from nearby sources to measured air concentrations or because of the contribution from the falling film at the clarifier.

GCA also performed an analysis on an aerated lagoon at Site 7.[14] This lagoon was covered and was purged with air at a rate of 1.4 m^3/s (3,000 ft^3/min). Predicted and calculated values for the mass transfer coefficients are given in Table 8-9 and show that predicted values are 1 to 2 orders of magnitude higher. The basis of the predicted values includes Thibodeaux and Reinhardt's correlations for aerated systems. No strong conclusions on the model's validity can be drawn from these data because the dome enclosure over the system and its evacuation rate probably have a direct effect on emissions. In addition, difficulties with air measurements and determination of the appropriate driving-force concentration (assumed to be the bulk liquid concentration) can lead to errors in the calculated values of the overall mass transfer coefficient.

The results of the biodegradation model were also compared to available data from biodegradation measurements. The most desirable comparison would be for a system in which the air emission rate and biodegradation rate were measured directly. However, the extent of biodegradation from studies of real systems has usually been determined by difference from a material balance (what enters the system minus what leaves with the effluent and with air emissions).

TABLE 8-9. COMPARISON OF RESULTS FOR COVERED AERATED LAGOON AT SITE 7[15,16]

	Mass transfer coefficient (x 10^4 m/s)	
Constituent	Vent rate measurement	Predicted[a]
1,2-Dichloroethane	0.05	7.2
Benzene	0.30	8.9
Toluene	0.95	8.8

[a] Based on an estimated windspeed (not measured) of 5 m/s[17] and an estimated turbulent area of about 50 percent.[18]

Petrasek et al. performed such a study on a large pilot-scale activated sludge system with diffused air aeration.[19] The activated sludge unit was enclosed, and the diffused air that was removed was sampled (for flow rate and concentration) to determine air emissions. This system was designed for a flow rate of 2.2 L/s (35 gal/min) with an air purge rate of 57 L/s. A summary of the operating parameters is given in Table 8-10. The study used a synthetic wastewater that contained individual volatile compounds at levels of 32 to 300 ppb. The biomass concentration was 2 g/L, and the resultant food-to-microorganism (F/M) ratio of 0.5 is well within the recommended design range of 0.2 to 0.6.

Petrasek reported the percent of each compound entering the activated sludge unit that was emitted with the diffused air. The results are summarized in the first column of Table 8-11 and show a range of measured values from 5 percent for chlorobenzene to 62 percent for 1,1,1-trichloroethane. The predictions of the biodegradation model discussed in Section 4.0 are presented in the second column for comparison. The third column in the table lists the biorates that were used from the data base (CHEMDAT6, primarily from Pitter[22]). The comparison shows that the model predictions for percent emitted are higher than the measured values for those compounds in the data base that were assigned biorates of zero, generally as a default value.

Tabak et al.[23] conducted an extensive study of the biodegradability of several toxic compounds, including the chlorinated compounds in Table 8-11 with assigned biorates of zero. Although they did not measure biodegradation rate constants, they found that these compounds, when evaluated in a properly acclimated system, could be biodegraded. Several of these compounds required a gradual adaptation of the biomass and were difficult to biodegrade; however, they concluded that the compounds were potentially biodegradable. Because Petrasek's data also indicated that these compounds were biodegradable, the biorate from the mathematical model was determined that would estimate the fraction emitted to match the measured fraction emitted. These estimates are presented in the fourth column of Table 8-11. The estimated biorates from this back calculation are about the same order of magnitude as the non-zero values in the data base, except for toluene. Note that relatively tight range of 1.1 to 1.8 g/s per g biomass for six compounds, with a value of 1.5 for three compounds.

TABLE 8-10. DESCRIPTION OF PETRASEK'S ACTIVATED SLUDGE SYSTEM[20]

Parameter	Value
Flow rate (L/s)	2.2
Volume (m^3)	59.8
Residence time (h)	7.5
Air rate (L/s)	57
Biomass concentration (g/L)	2.0
Concentration range for organics (ppm)	0.032 - 0.30
F/M[a]	0.5

[a] F/M[a] = Food to microorganism ratio (lb/lb biomass • day) based on chemical oxygen demand.

TABLE 8-11. COMPARISON OF PETRASEK'S MEASUREMENTS AND MODEL PREDICTIONS

Compound	Percent emitted		Biorates, g/s per g biomass x 10^8	
	Measured[21]	Predicted[a]	Data base[b]	To match measurements[c]
Chloroform	34	31	0.81	0.75
Carbon tetrachloride	59	97	0	1.5
Trichloroethylene	41	91	0	1.1
1,1,2-Trichloroethane	25	44	0	0.36
Benzene	15	2	5.3	1.8
1,1,1-Trichloroethane	62	97	0	1.3
Chlorobenzene	5	60	0.41	2.6
Tetrachlorobenzene	27	97	0	2.8
Toluene	20	0.2	20.0	1.5
Ethylbenzene	21	87	12.9	1.5

[a] Based on the model in Section 4.0.

[b] From the data base of biorates accompanying this report (see Appendix A).

[c] This is the biorate, when used in the mathematical model, that would predict a fraction emitted that exactly matches the measured fraction emitted.

Another type of comparison between measurements and predictions involves effluent concentrations for well-defined wastewater treatment systems. Namkung and Rittman[24] reported influent and effluent concentrations of volatile organics for two Chicago wastewater treatment plants that receive large shares of industrial discharges. The measurements were made for two large activated sludge units aerated by diffused air. In addition, the system's operational parameters were defined (Table 8-12) and provided the necessary inputs for the mathematical model that includes air emissions (diffused air system) and biodegradation. The total volatile organic concentration was also provided, and the only significant assumption needed was an average biorate for the mixture. For this analysis, an average biorate equal to that of benzene from the data base was used (5.3×10^{-6} g/s per g biomass).

The results of measured and predicted effluent concentrations are summarized in Table 8-13. The most convincing comparison is the close match for both plants for tetrachloroethylene, which the authors stated was not biodegradable in these systems. Therefore, a biorate equal to zero was used in the model for this compound. The close agreement between measured and predicted effluent concentrations suggests that this compound is almost entirely removed by air stripping, and the quantity predicted to be air stripped by the model is reasonably accurate.

The results in Table 8-13 also indicate that 1,1,1-trichloroethane and trichloroethylene are biodegraded. The model predictions used a biorate for these two compounds that was derived from Petrasek's data in Table 8-11. Both Petrasek's data and the comparison in Table 8-13 indicate that these compounds are biodegraded to some extent; otherwise, the measured effluent concentrations in Table 8-13 would have been higher than those predicted by the model with biodegradation included.

Another comparison that can be made is based on a study of Kincannon and Stover and biorates derived from their experimental data.[27] In their study, relatively high concentrations of individual compounds (up to 258 ppm) and a high F/M ratio were used in a laboratory-scale activated sludge system (3 L). Because of the relatively high concentrations and resultant F/M ratio, the biodegradation rate may be described by zero-order kinetics

TABLE 8-12. DESCRIPTION OF TWO CHICAGO ACTIVATED SLUDGE UNITS[25]

	Calumet	West-southwest
Volume (m^3)	184,500	802,300
Wastewater flow (m^3/s)	10.0	36.6
Air rate (m^3/s)	55	193
Residence time (h)	5.1	6.1
Biomass (g/L)	2.2	2.0
Concentrations (ppb)		
Chloroform, in	4.0	4.4
out	7.1	2.4
Ethylbenzene, in	18	10
out	0.5	BDL
Methylene chloride, in	9.8	48
out	11	11
Tetrachloroethylene, in	16	12
out	2.1	1.6
Toluene, in	85	22
out	6.2	BDL
1,1,1-Trichloroethane, in	13	15
out	2.9	2.2
Trichloroethylene, in	9.7	22
out	0.5	2.1

BDL = Below detection limit.

TABLE 8-13. COMPARISON OF MEASURED AND PREDICTED EFFLUENT CONCENTRATIONS FOR CHICAGO WASTEWATER TREATMENT PLANTS[26]

Compound	Biodegradable[a]	Calumet effluent concentrations, ppb		West-southwest effluent concentrations, ppb	
		Measured	Predicted	Measured	Predicted
Chloroform	Yes	b	b	2.4	2.3
Ethyl benzene	Yes	0.5	2.3[c]	d	1.2[c]
Methylene chloride	Yes	b	b	11	15.6
Tetrachloroethylene	No	2.1	2.1	1.6	1.7
Toluene	Yes	6.2	5.4	d	1.3
1,1,1-Trichloroethane	Yes	2.9	3.2[e]	2.2	3.7[e]
Trichloroethylene	Yes	0.5	2.7[e]	2.1	6.3[e]

[a] Yes means that Petrasek found some biodegradation (see Table 8-11). No means that the compound is not biodegradable.

[b] No comparison possible because measured concentration in effluent was greater than measured concentration in influent.

[c] Based on biorate derived from land treatment studies.

[d] Measured effluent concentration was below detection limit.

[e] Adjusted by changing biorates. The ratio of the compound's biorate to toluene's biorate from Petrasek's data in Table 8-11 was used. (For example, the value used for trichloroethylene is 1.1/1.5 x 20).

instead of the first-order kinetics on which the model is based. Kincannon presented information on influent and effluent concentrations, biomass concentrations, reactor volume, and residence time. These data were used to estimate zero-order rate constants for acrolein, methylene chloride, benzene, 1,2-dichloroethane, and 1,2-dichlorobenzene in our current data base. A similar analysis was performed for nitrobenzene, acrylonitrile, ethyl acetate, and phenol to compare Kincannon's results with those from Pitter. The comparison shown in Table 8-14 indicates that Pitter's results from a batch system are comparable to the results from Kincannon's flow-through system. Because Kincannon's system is apparently described by zero-order kinetics, the model presented in Section 4.0 does not apply to Kincannon's system because the model is based on first-order kinetics.

A separate study was conducted for EPA to evaluate measured and predicted emissions for aerated waste treatment systems.[29] The correlations of Thibodeaux and Reinhardt were used (as recommended in Section 4.0) to estimate the mass transfer coefficients of the turbulent zone. The results showed an agreement between measured and predicted values that were within an order of magnitude. The report concluded that, when adequate descriptions of plant operating parameters are available, reliable emission estimates can be obtained from the models (within the accuracy that results from variations in sampling and chemical analysis). When plant operating parameters are known, the major limitations in the models result from a lack of accurate biooxidation rates and vapor/liquid equilibrium data for specific compounds.[30]

8.2.3 Recommendations for Additional Data

The estimate of emissions from open liquid surfaces is provided by the product of the mass transfer coefficient, driving-force concentration, and surface area. Surface area can be determined with reasonable accuracy. The previous comparison of mass transfer coefficients indicated that they can be estimated within an order of magnitude. Probably the greatest source of uncertainty is in the estimate of the appropriate driving force for mass transfer. The concentration is likely to vary with time and location in the impoundment. The type of flow system and extent of mixing in the liquid also will affect this concentration.

TABLE 8-14. COMPARISON OF BIORATES

	Biorates ($\times 10^6$ g/s per g biomass)	
Compound	Data base	Calculated from Reference 28[a]
Nitrobenzene	1.9	1.4 - 4.1
Acrylonitrile	12	>7.9
Ethyl acetate	4.9	6.0 - 9.3
Phenol	9.3	>9.1

[a] Greater than implies rate could be higher because the concentration in the effluent was below detection limit.

For the less volatile compounds that may be controlled by gas-phase mass transfer, the collection of equilibrium data may be useful to compare with the estimated values used in the models. The comparisons presented in this section primarily address compounds with high volatility in water (high Henry's law constant). Because semivolatile compounds also can be emitted to a significant extent, air emission measurements for these less volatile compounds would be useful for comparison with model predictions.

8.3 LAND TREATMENT

Field data from four test sites and one laboratory simulation were used as a basis for comparing measured emissions with estimated emissions using the RTI land treatment model. Two other laboratory simulations of land treatment are under way or near completion, but the documentation on those tests is not yet sufficiently complete so that comparisons of measured and estimated emissions can be made. These include an EPA-sponsored study being conducted by Radian Corporation and a simulation study by Chevron Research Company in Richmond, California. Table 8-15 summarizes the tests evaluated. Generally, estimated emissions are within an order of magnitude of measured values. Values of estimated emissions varied both above and below measured values.

Comparisons of estimated and measured emission flux rates are presented graphically in this section. Comparisons of estimated and measured emissions by weight percent of applied material are presented in the next section.

Considering the potential for error in measuring or estimating values for parameters that are input to the model and the potential for error in measuring emissions, differences in the range of an order of magnitude are not unexpected. In making the comparisons, values for all model inputs sometimes were not available in the emission test reports. In these cases, values were estimated using averages of field data or values identified previously as typical or representative of actual land treatment practices.

In the 1985 test at a Midwest petroleum refinery (Case 1),[31] emission measurements were made at sample locations in six test plots. For each plot, emission measurements were made after waste application but before the plot was tilled, again after the waste was tilled, and for another period after a second tilling. All measurements were made using a flux

TABLE 8-15. SUMMARY OF LAND TREATMENT TESTING AND TEST RESULTS

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results	
							Waste constituent	Emissions, wt. %
12	West Coast corporate research facility	Laboratory simulation	1986 - 1987	Private corporation	Run 1 (raw waste)	2.5 months	Oil	35
					Run 2 (raw waste)	22 days	Oil	11
					Run 2 (treated waste)	22 days	Oil	1
13	Southwest research facility	Laboratory simulation	1986	EPA	Run 1[a] (API separator sludge)	31 days		
					Box #1		Oil	5.2
					Box #2		Oil	NA
					Box #3		Oil	6.5
					Box #4		Oil	6.7
					Run 2[a] (IAF float)	31 days		
					Box #1		Oil	15
					Box #2		Oil	NA
					Box #3		Oil	18
					Box #4		Oil	19
14	Midwestern refinery	Flux chamber	1985	ORD	Plot A	8 days	Benzene	81
							Toluene	41
							Ethylbenzene	195
							p-Xylene	16
							m-Xylene	39
							o-Xylene	28
							Naphthalene	1
					Plot B	8 days	Benzene	110
							Toluene	66
							Ethylbenzene	402
							p-Xylene	21
							m-Xylene	83
							o-Xylene	38
							Naphthalene	2

See notes at end of table.

(continued)

TABLE 8-15 (continued)

							Test results	
Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Waste constituent	Emissions, wt. %
14 (con.)								
					Plot C	8 days	Benzene	39
							Toluene	17
							Ethylbenzene	140
							p-Xylene	25
							m-Xylene	25
							o-Xylene	17
							Naphthalene	
					Plot D	8 days	Benzene	142
							Toluene	86
							Ethylbenzene	353
							p-Xylene	55
							m-Xylene	79
							o-Xylene	52
							Naphthalene	2
					Plot E	8 days	Benzene	107
							Toluene	63
							Ethylbenzene	345
							p-Xylene	43
							m-Xylene	52
							o-Xylene	39
							Naphthalene	1
					Plot F	8 days	Benzene	84
							Toluene	47
							Ethylbenzene	208
							p-Xylene	13
							m-Xylene	28
							o-Xylene	24
							Naphthalene	1
15	West Coast refinery	Flux chamber	1984	ORD	Surface application	5 weeks	n-Heptane	60
							Methylcyclohexane	61
							3-Methyl-heptane	52
							n-Nonane	56
							1-Methylcyclohexene	49
							1-Octene	50
							β-Pinene	17
							Limonene	22

See notes at end of table.

(continued)

TABLE 8-15 (continued)

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results: Waste constituent	Test results: Emissions, wt. %
15 (con.)							Toluene	37
							p-,m-Xylene	35
							1,3,5-Trimethylbenzene	21
							o-Ethyl-toluene	32
							Total VO	30
							Total oil	1.2
					Subsurface	5 weeks	n-Heptane	94
							Methylcyclohexane	88
							3-Methyl-heptane	77
							n-Nonane	80
							1-Methylcyclohexane	76
							1-Octene	74
							β-Pinene	21
							Limonene	26
							Toluene	56
							p-,m-Xylene	48
							1,3,5-Trimethylbenzene	27
							o-Ethyl-toluene	42
							Total VO	36
							Total oil	1.4
16	Southwest research facility	Laboratory simulation	1983	API/EPA	Run no. 18	8 hours[b]	Oil	9.1
					Run no. 21		Oil	4.4
					Run no. 24		Oil	0.02
					Run no. 27		Oil	0.6
					Run no. 28		Oil	0.1
					Run no. 32		Oil	3.0
					Run no. 33		Oil	2.6
					Run no. 34		Oil	0.01
					Run no. 35		Oil	0.9
					Run no. 36		Oil	78.8
					Run no. 37		Oil	9.9
					Run no. 40		Oil	0.7
					Run no. 41		Oil	2.8
					Run no. 44		Oil	4.9
					Run no. 45		Oil	49.9
					Run no. 46		Oil	7.7
					Run no. 47		Oil	6.9
					Run no. 48		Oil	5.0
					Run no. 49		Oil	9.7
					Run no. 50		Oil	1.1
					Run no. 51		Oil	0.47

See notes at end of table.

(continued)

TABLE 8-15 (continued)

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results	
							Waste constituent	Emissions, wt. %
10	Gulf Coast commercial TSDF	Flux chamber	1983	ORD	Single test[c]	69 hours	Total VO	0.77
						50 hours	Benzene	3.91
17	Midwestern refinery	Flux chamber	1979	API	Centrifuge sludge			
					Test no. 5	19.9 hours	Oil	0.1
					Test no. 6	307 hours	Oil	2.5
					API separator sludge[d]			
					Test no. 7	619 hours	Oil	13.5
					Test no. 8	122 hours	Oil	1.1
					Test no. 9	520 hours	Oil	13.5

API = American Petroleum Institute.

IAF = Induced air flotation.

ORD = Office of Research and Development.

[a] Sludge applied to Box #1 and Box #3 as duplicate tests; sludge treated with mercuric chloride to eliminate (or reduce) bioactivity applied to Box #4 and no sludge applied to Box #2, which served as a control.

[b] Each run for which results are reported was 8 hours.

[c] Test was conducted using aged wastes.

[d] Allowed to weather for 14 days in open 5-gal buckets in an outdoor open shelter prior to application.

chamber and tenax traps. Emission rates were measured for six specific organic constituents: benzene, toluene, p-xylene, o-xylene, m-xylene, and naphthalene. Benzene and toluene were selected as a basis for comparing measured and estimated emissions in this test. The comparison was made for test plot A after the waste was tilled for the first time. Estimated emissions for each compound are higher than the measured values but generally are within a factor of 10. Estimated and measured values are shown graphically for benzene and toluene in Figures 8-1 and 8-2, respectively.

At the West Coast refinery (Case 2),[32] emission tests were made using three adjacent plots marked off in the land treatment site. The center plot was used as a control and had no waste applied while waste was applied to the other two plots. One plot had waste applied to the soil surface and the other had waste applied by subsurface injection. Flux chambers were situated on each test plot and emission measurements were made during three different test periods each lasting 4 days. Canister air samples, sludge samples, and liquid samples were analyzed by gas chromatography (GC). Emissions of both total VO and selected specific constituents were measured during the test. For comparing measured and estimated emissions, total VO and toluene emissions from the surface application plot were used. Estimated emission rates for both toluene and total VO agree reasonably well with measured rates but range from higher to lower than measured rates at different times. Estimated cumulative emissions over the entire test period agree reasonably well with the measured values. For both toluene and total VO, estimates covered a 4-day period with a till occurring after 2 days. Estimated and measured values over the 4-day period for which the comparison is made are generally within an order of magnitude, as can be seen in Figures 8-3 and 8-4. Measured values were reported as half-day average emission rates.

For the test at the commercial hazardous waste site in 1983, (Case 3),[33] waste was applied to a single test plot and tilled into the soil. Air emission measurements were made over a 3-day period using a flux chamber and gas canisters. Sampling locations were selected randomly, with a control point used to provide a common sampling position each day.

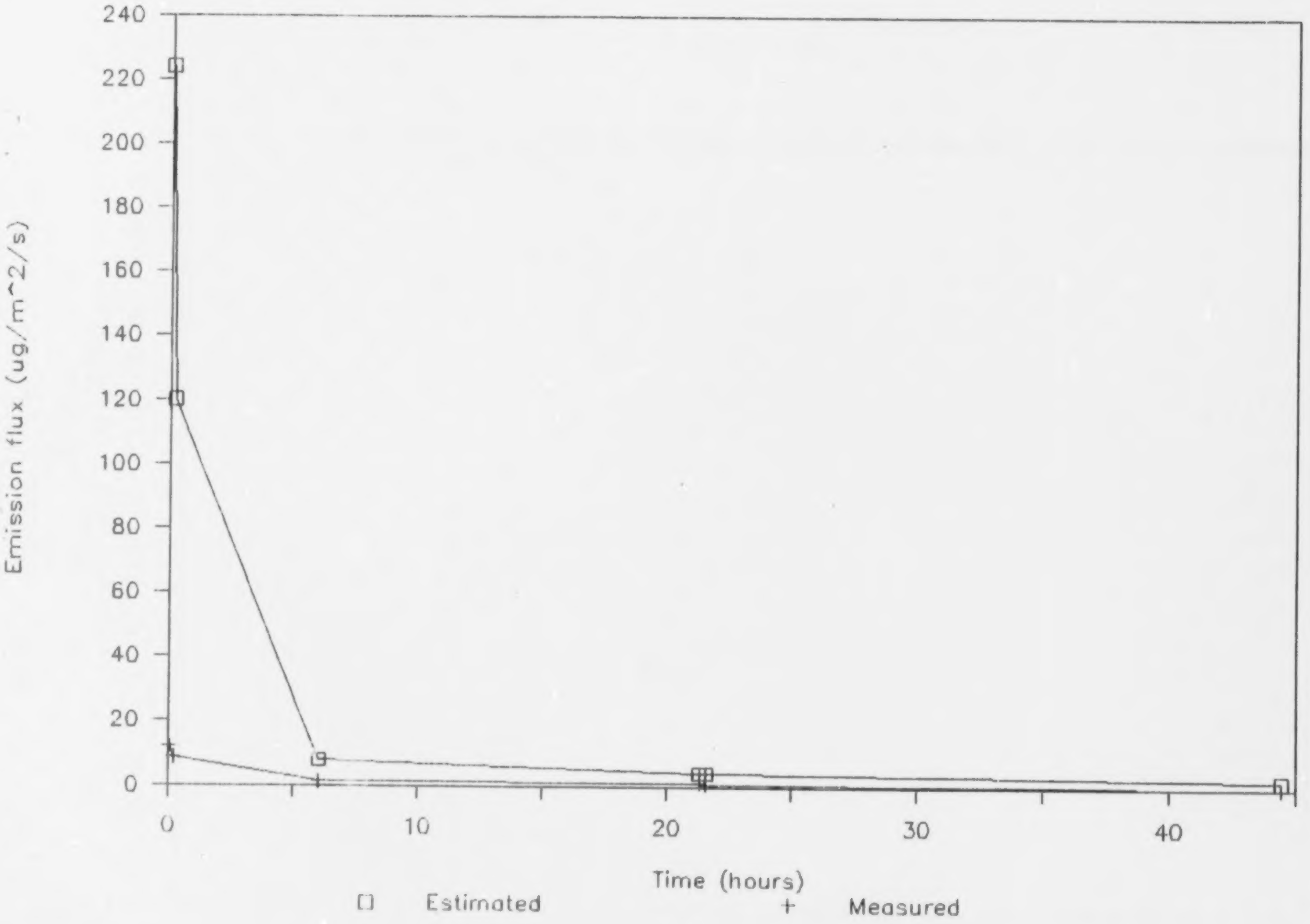

Figure 8-1. Estimated vs. measured benzene emission flux rates—Case 1.

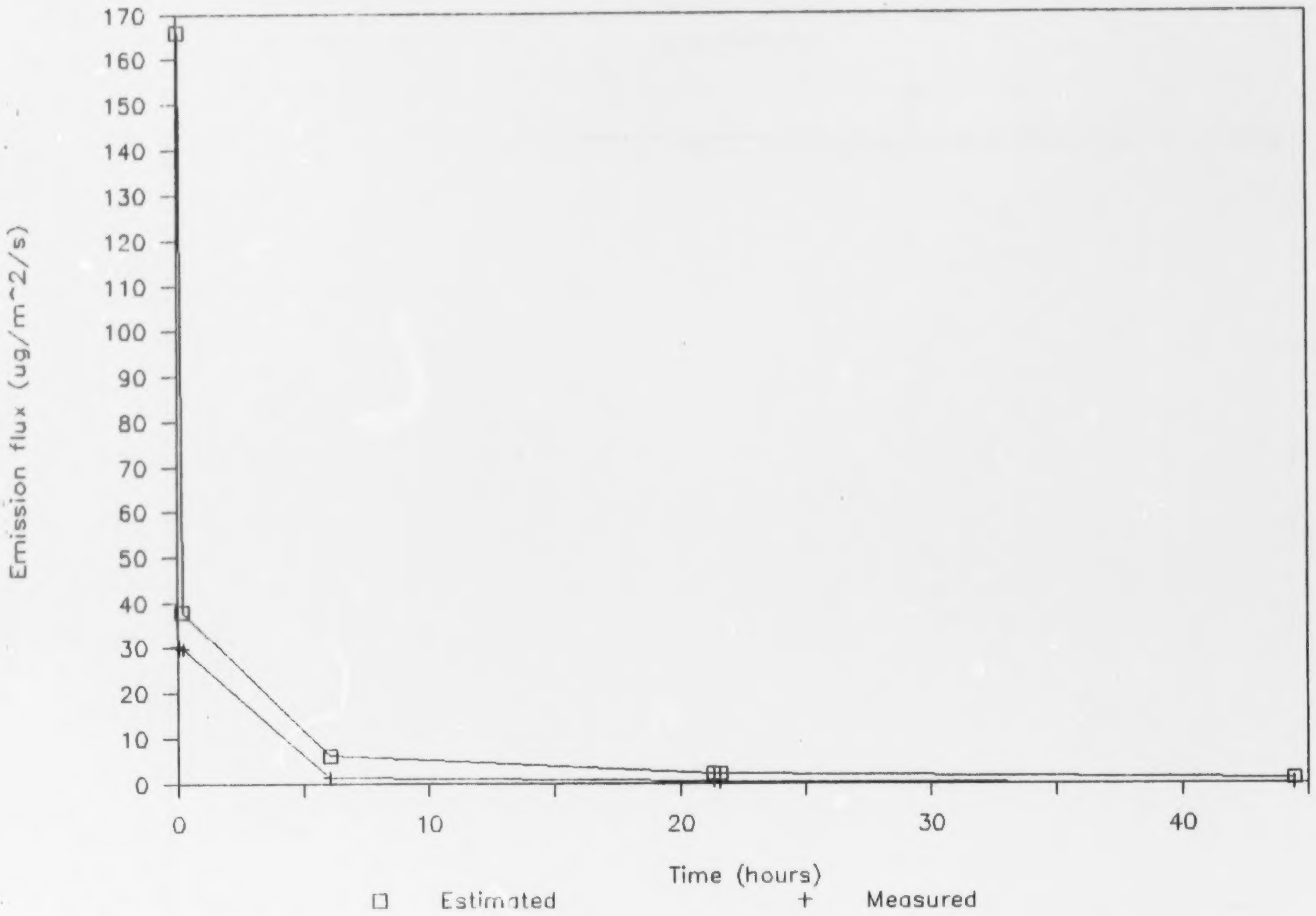

Figure 8-2. Estimated vs. measured toluene emission flux rates—Case 1.

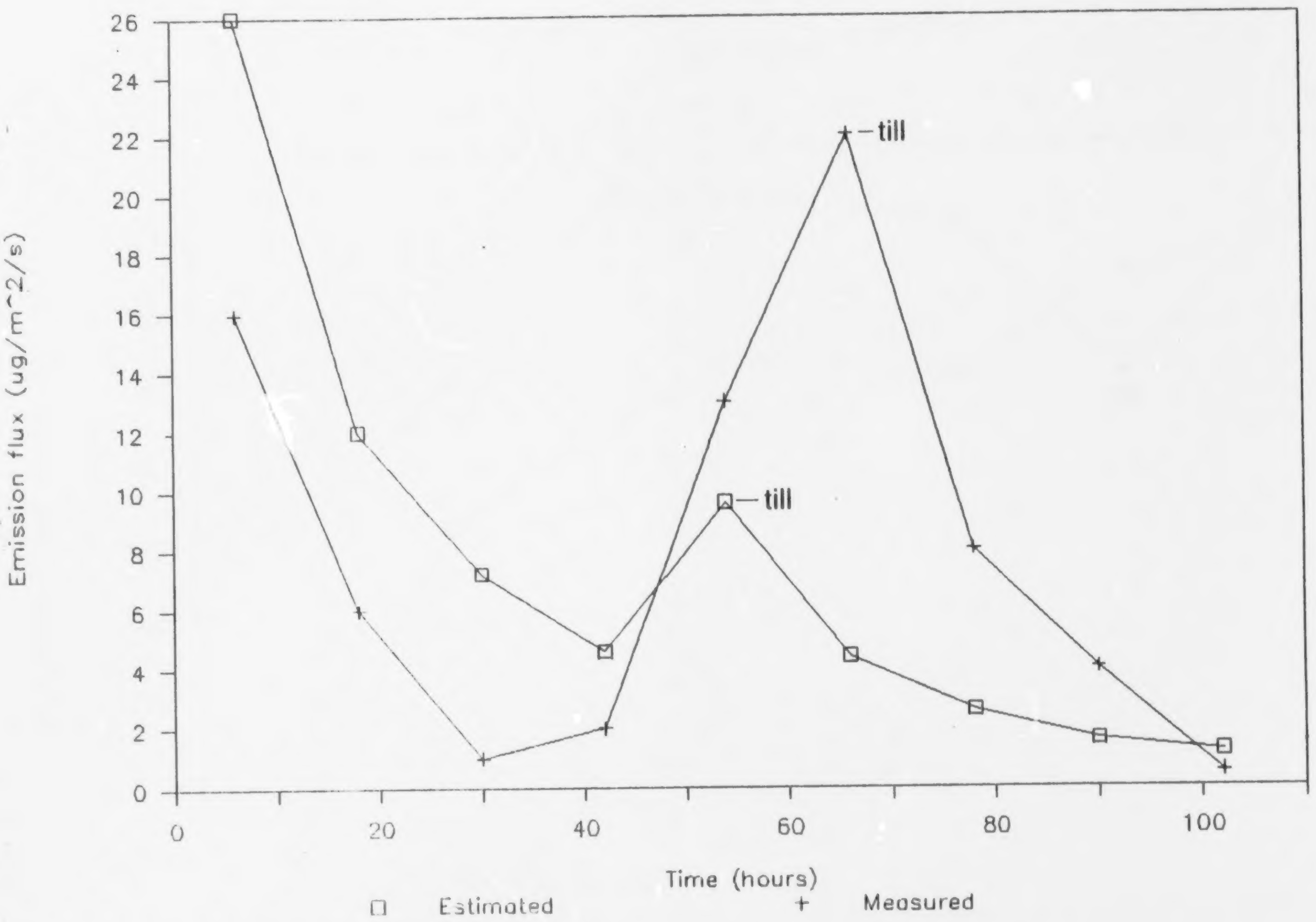

Figure 8-3. Estimated vs. measured toluene emission flux rates—Case 2 (data for 4 days only).

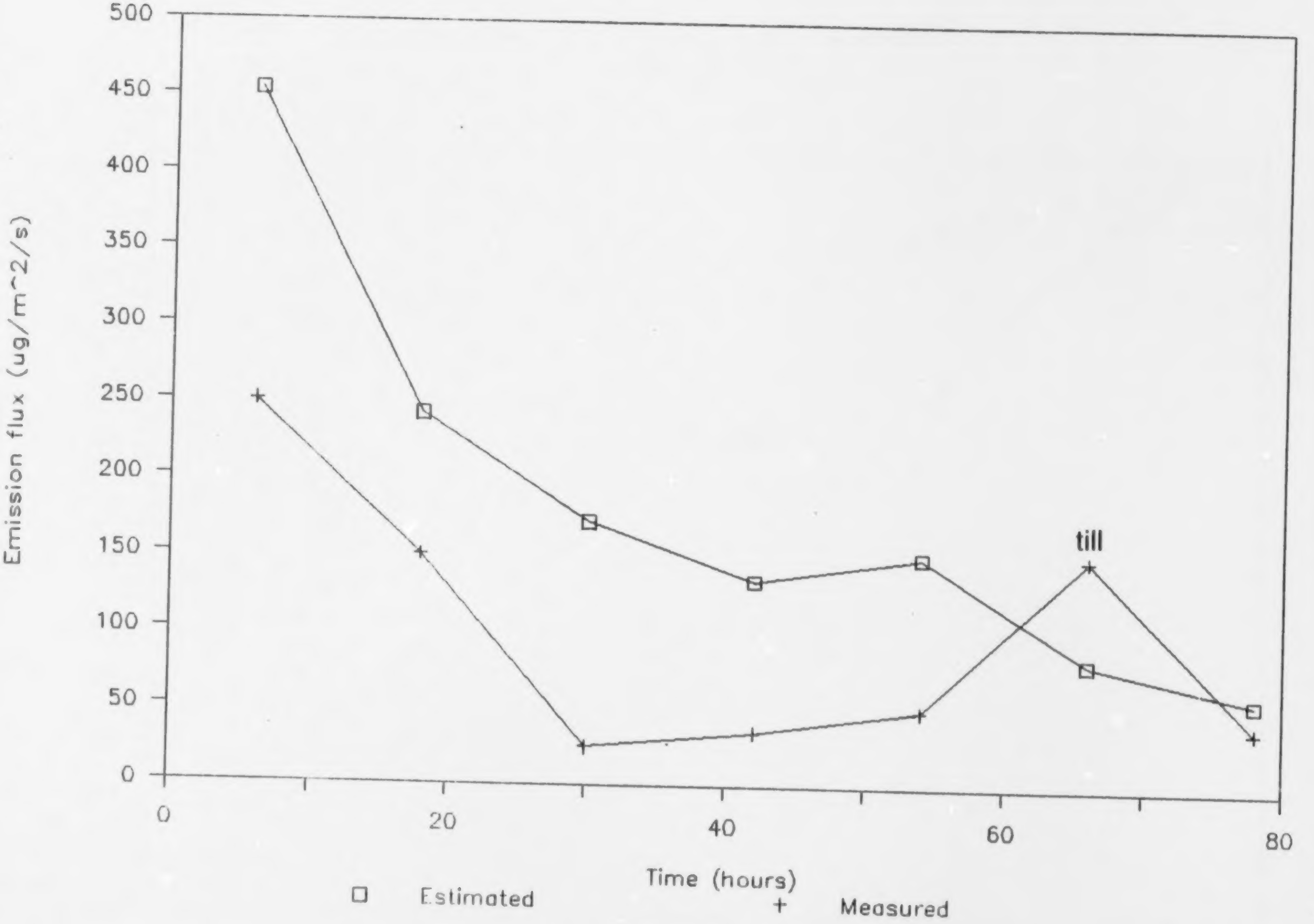

Figure 8-4. Estimated vs. measured total VO emission flux rates—Case 2.

Sample analyses were made by GC. Emission comparisons of measured and estimated emissions were made for total nonmethane hydrocarbon (NMHC) emissions using data generated by GCA in a separate study of the data from this test.[34] As with previous tests, estimated emission flux rates were greater than measured values but mostly were within a factor of 10 or less of the measurements. Estimated cumulative emissions also were substantially higher than measured values. Estimated and measured values of instantaneous emission flux rates are shown in Figure 8-5.

In the 1979 test at the Midwest petroleum refinery (Case 4),[35] three test plots were laid out. One plot was used as a control and had no waste applied, one plot had an API separator sludge applied, and the other plot had a centrifuge sludge applied. A 1-ft^2 collector box was placed on the test plot and continuously purged with fresh air. The outlet from the box was analyzed for total VO (as methane and NMHC) using a continuous hydrocarbon analyzer. For one test run, total VO emissions were estimated with the land treatment model for comparison with the measured values. Measured and estimated values are shown graphically in Figure 8-6. As can be seen, the estimated and measured values agree quite well for this test. Total cumulative emissions for each test were also estimated using the model and compared with measured values. The estimated values were generally higher than measured values for these emissions.

8.3.1 Midwest Refinery--1985 (Case 1)

Table 8-16 presents the model input values used to compare estimated and measured emissions for plot A of the Case 1 test data. The information in Table 8-16 represents data for plot A as reported in the test report. Similar information was reported for plots B through F and those data were used as appropriate for input to the model. Table 8-17 shows measured emissions of six constituents made during the test. In this test, the waste was allowed to stay on top of the soil for 24 hours before it was tilled into the soil. Measured emissions during the first 24 hours were combined with measured emissions after tilling to get total emissions. Table 8-17 shows variations in measured emissions among the different test plots and shows emissions greater than applied material for some plots and some waste constituents. In Table 8-17, weight fraction represents the fraction of applied material that is emitted to the air. For ethylbenzene,

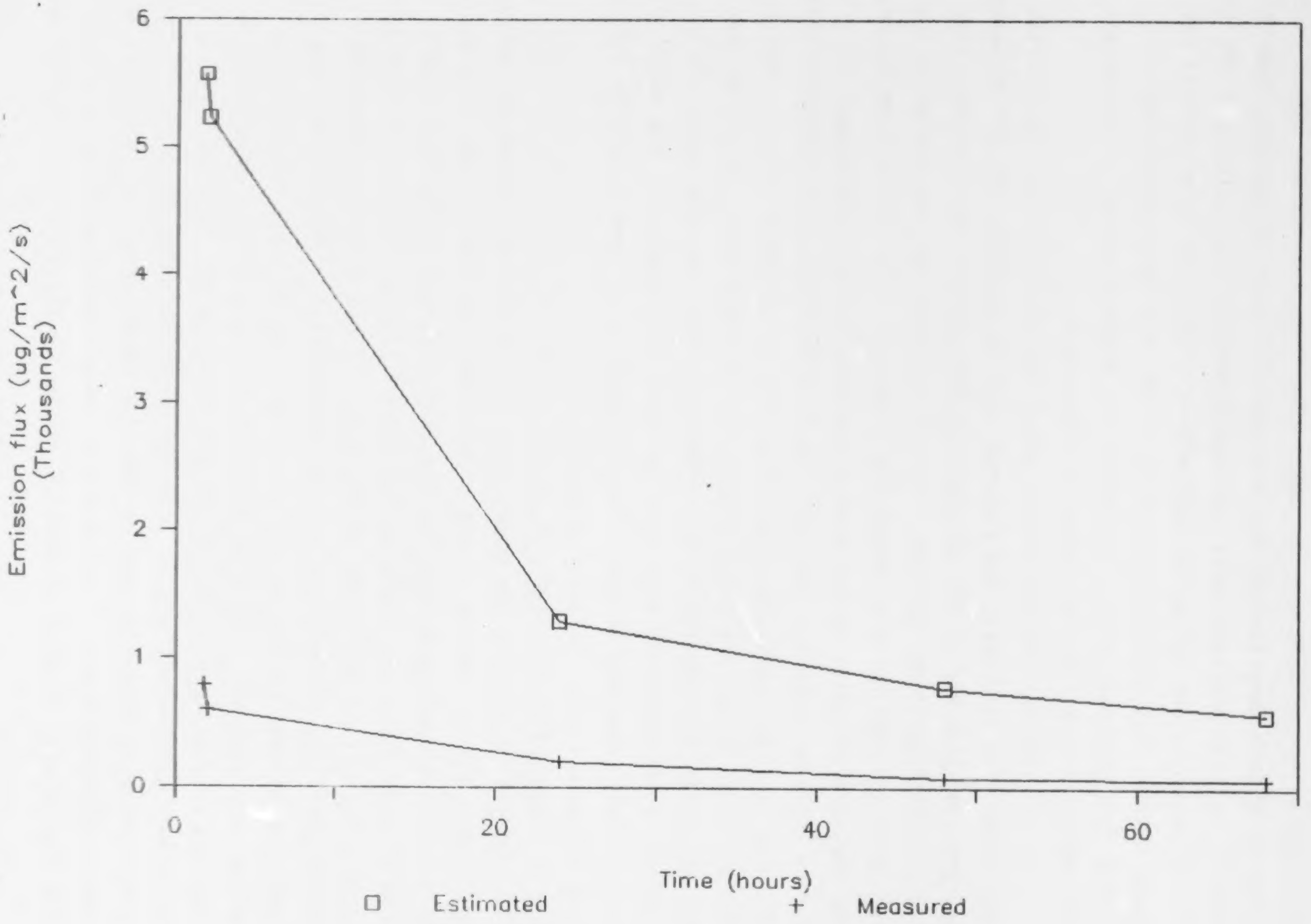

Figure 8-5. Estimated vs. measured VO emission flux rates—Case 3.

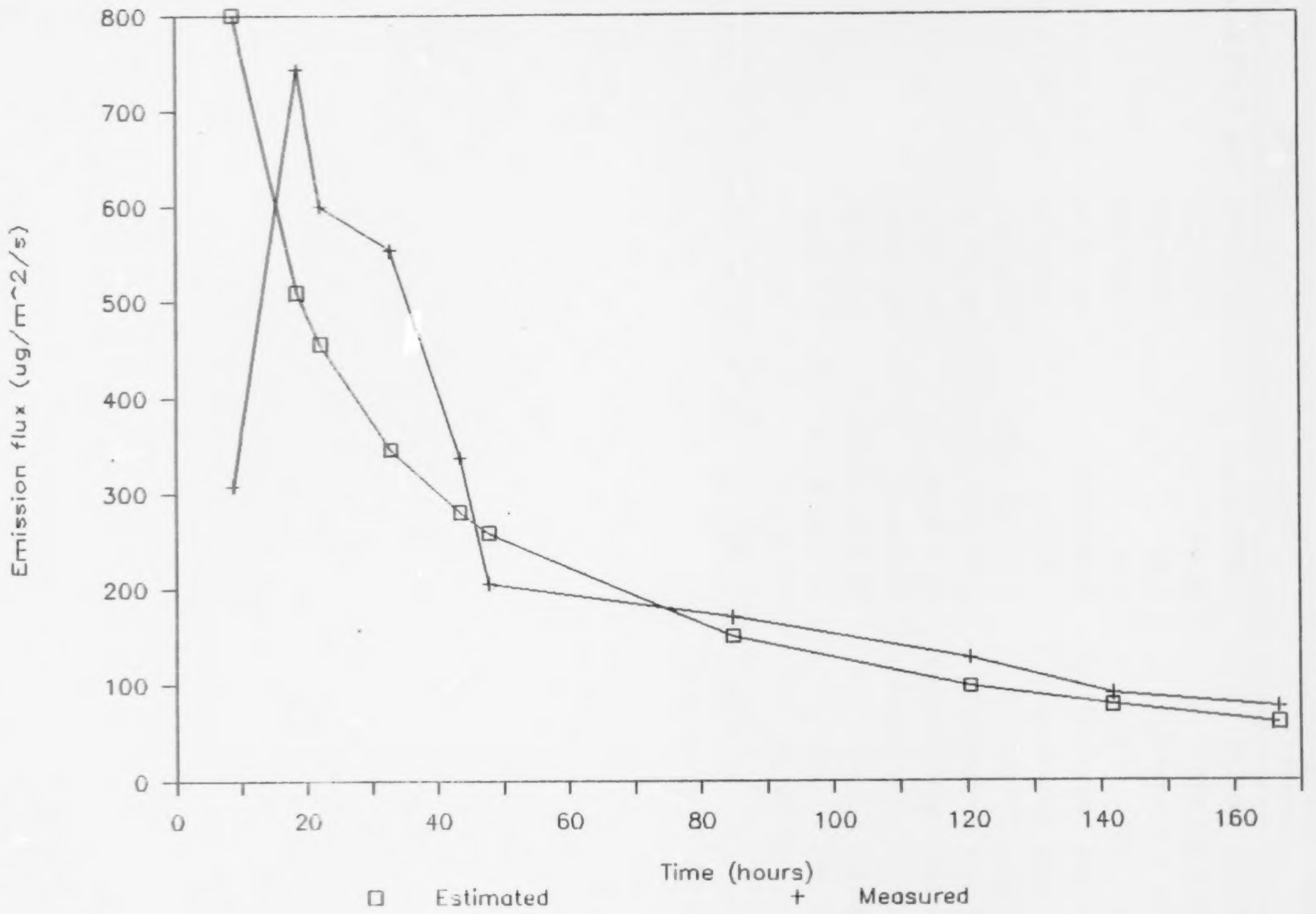

Figure 8-6. Estimated vs. measured emission flux rates—Case 4.

TABLE 8-16. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic loading	0.0236 g/cm^3	Calculated from field data
Tilling depth	20 cm	Field data
Soil air porosity	0.40	Field data
Soil total porosity	0.61	Field data
Benzene concentration[b]	0.000249	Calculated from field data
Toluene concentration[b]	0.000632	Calculated from field data
Benzene diffusivity	8.80 E-02 cm^2/s	Data base
Toluene diffusivity	8.70 E-02 cm^2/s	Data base
Benzene vapor pressure	95.2 mm Hg	Data base
Toluene vapor pressure	30.0 mm Hg	Data base
Benzene biorate	19.0 mg VO/g•h	Data base
Toluene biorate	73.0 mg VO/g•h	Data base
Molecular weight of oil	282 g/g mol	Assumed

[a] Source of field data: Reference 36. Data represent conditions in plot A.

[b] Weight fraction of oil.

TABLE 8-17. MEASURED AND ESTIMATED EMISSIONS--CASE 1

	Measured cumulative emissions[a]													
	Benzene		Toluene		Ethylbenzene		p-Xylene		m-Xylene		o-Xylene		Naphthalene	
Test location	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.
A	271.01	0.81	340.71	0.41	67.97	1.95	7.39	0.16	96.40	0.39	21.11	0.20	2.15	0.01
B	299.00	1.10	464.20	0.66	96.40	4.02	7.60	0.21	103.84	0.83	23.10	0.30	2.31	0.02
C	100.36	0.39	209.90	0.17	59.27	1.40	16.03	0.26	87.17	0.25	10.76	0.17	3.00	0.01
D	459.42	1.42	703.00	0.86	101.05	3.53	23.92	0.65	106.32	0.79	30.02	0.62	3.35	0.02
E	302.23	1.07	576.10	0.63	109.31	3.45	20.74	0.43	130.39	0.52	31.56	0.39	2.46	0.01
F	324.00	0.84	464.97	0.47	71.66	2.00	6.07	0.13	70.04	0.20	21.39	0.24	2.44	0.01

	Estimated cumulative emissions			
	Benzene		Toluene	
Test location	μg/cm^2	wt. frac.	μg/cm^2	wt. frac.
All	--	0.03	--	0.53

[a] Test duration was approximately 8 days.

all plots have measured emissions in excess of the amount applied. To compare measured and estimated emissions, the RTI land treatment model can be used for estimating emissions both before and after tilling. Estimated cumulative emissions for benzene and toluene for all plots are shown in Table 8-17 and show reasonable agreement with measured values.

8.3.2 West Coast Refinery (Case 2)

The data in Table 8-18 were used to estimate emissions of toluene and total VO from the surface application plot at the Case 2 land treatment facility. Estimated and measured cumulative emissions are compared in Table 8-19. The comparisons were made for total VO (as determined by purge and trap) and for toluene.

8.3.3 Commercial Waste Disposal Test (Case 3)

Table 8-20 shows the inputs used to estimate emissions from the Case 3 land treatment operation. No specific constituent data were available so emissions were estimated using average characteristics of the total organic phase. Results are shown in Table 8-21. The comparison is made for the estimated versus measured cumulative weight percent of applied oil that is emitted after 24 hours and after 68 hours, which is the duration of the entire test.

8.3.4 Midwest Refinery--1979 (Case 4)

The information in Table 8-22 was used to estimate emissions from the Case 4 facility test. No specific constituent data were available; emissions were estimated for total organics using average parameter values. Results are presented in Table 8-23. The comparisons are for the cumulative weight percent of applied oil that was emitted over the entire period of each test.

8.4 LANDFILLS AND WASTEPILES

Emission testing has been performed on at least one active (open) landfill at each of five sites. Only three of these sites have closed or inactive landfills at which emission measurements were performed. No emission test data are available for wastepiles.

TABLE 8-18. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic (oil) loading	0.0328 g/cm^3	Estimated from field data
Tilling depth	20 cm	Field data
Soil porosity	0.5	Field data
Molecular weight of oil	282 g/g mol	Field data
Toluene concentration	0.00157 (wt. fraction of oil)	Calculated from field data
Toluene diffusivity	8.70 E-02 cm^2/s	Data base
Toluene vapor pressure	30.0 mm Hg	Data base
Toluene biorate	73.0 mg VO/g•h	Data base
VO concentration	0.04 (wt. fraction of oil)	Calculated from field data
VO diffusivity	6.60E-02 cm^2/s	Average from field data
VO vapor pressure	14.6 mm Hg	Average from field data
VO biorate	23.68 mg VO/g•h	Average from field data

[a] Source of field data: Reference 37.

TABLE 8-19. ESTIMATED VS. MEASURED EMISSIONS--CASE 2

	Time after tilling, day/h	Estimated emissions, wt. %	Measured emissions, wt. %
Toluene	33/793	31	37
Total VO	33/793	32	30
Total oil	33/793	1.3	1.2

TABLE 8-20. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic loading	0.0406 g/cm^3	Calculated from field data
Tilling depth	19.6 cm	Field data
Soil porosity	0.5	Assumed
Molecular weight of oil	282 g/g mol	Assumed
Vapor pressure	0.57 mm Hg	Calculated by GCA[b]
Diffusivity in air	2.70 E-02 cm^2/s	Average from field data
Biorate	23.68 mg VO/g•h	Average from data base

[a] Source of field data: Reference 38.

[b] Reference 39.

TABLE 8-21. ESTIMATED VS. MEASURED TOTAL VO EMISSIONS--CASE 3

Time after tilling, h	Estimated emissions, wt. % total applied oil	Measured emissions, wt. % total applied oil
68.00	4.5	0.77

TABLE 8-22. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic loading	0.002125 g/cm^3	Estimated from field data
Tilling depth	20 cm	Assumed
Soil porosity	0.5	Assumed
Molecular weight of oil	282 g/g mol	Assumed
Diffusivity in air	9.12 E-02	Average from data base
Vapor pressure	0.76 mm Hg	Calculated by GCA[b]
Biorate	23.68 mg VO/g•h	Average from data base

[a] Source of field data: Reference 40.

[b] Reference 41.

TABLE 8-23. ESTIMATED VS. MEASURED EMISSIONS--CASE 4

Test	Elapsed time, day/h	Estimated emissions, wt. % total applied oil	Measured emissions, wt. % total applied oil
5	1/20	5.0	0.14
6	13/307	14.0	2.5
7	26/619	16.0	13.5
8	5/122	14.0	1.1
9	22/520	28.0	13.4

Meaningful comparisons can be performed of emission test data with mathematical model predictions provided that all key model input parameters are available from the tests. A review of documentation from the emission tests indicates that generally more than half of the needed model input parameters (other than chemical property data) are unknown, despite the fact that several emission tests were performed with the stated intention of validating emission models. Examples of key model input parameters that are generally unknown or poorly defined include waste porosities (air and total), average waste bed temperature (for active and closed landfills), waste composition at depths greater than the surface layer, barometric pressures, clay cap porosities (air and total), clay cap thickness, waste bed depth, and (for active landfills particularly) time between core sampling and air emissions determination. To apply the models, representative default values have been used where necessary. Because of the necessity to estimate key input parameters, the comparisons that follow are of extremely limited value for model validation. To achieve validation of emission models, additional field tests or laboratory experiments are needed for active and closed landfills and wastepiles.

Field data from two sites were used for comparison with the land treatment model as applied to active landfills. These sites (5 and 8) were chosen because of similarity in constituency of selected chemicals and relative availability of model input parameters. However, it should be noted that at each of the sites more than half of the needed model input parameters were not available from the tests and thus required estimation.

Information on the waste composition within closed landfills was insufficient to allow use of the closed landfill model. At two of the three closed/inactive landfill sites (4 and 5), no solid samples of waste were taken; at the remaining site (Site 9), a single soil core was apparently extracted from the 3-ft clay cover, providing no information about the composition of the waste below the cover. However, it should be noted that Farmer et al.[42] (who developed the precursor* to the RTI closed landfill model) mentioned that their model has received experimental verification via a laboratory experiment using hexachlorobenzene-containing waste in a simulated landfill.

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*The Farmer et al. model accounts for diffusion through the clay cap only (not barometric pumping).

Following are the results of the comparison for active landfills at Sites 5[43,44] and 8[45]. Table 8-24 presents model input parameters used in the application of the RTI land treatment model to an active landfill at Site 5. Table 8-25 presents a comparison of measured and predicted emission rates for the Site 5 landfill.

Model predictions for the chemicals assessed here are higher than field data values by a factor ranging from 13 to 441. This discrepancy may be largely a result of the presence of daily earth covers (6 in. thickness) and layers of drums within the waste bed--neither of which are accounted for by the model. Other contributing factors may include the estimation of key model input parameters (e.g., air porosity of waste, temperature of the constituent within soil) and the nonrepresentative nature of the waste sample (obtained at the surface) for describing the waste composition at depth.

Table 8-26 presents model input parameters used in the application of the RTI land treatment model to an active landfill at Site 8. Table 8-27 presents a comparison of measured and predicted emission rates for the Site 8 landfill.

Model predictions of the emissions at Site 8 are, in general, closer to field data than were the predictions made for Site 5. Better overall agreement may be due to the absence of drums and daily earth covers in this landfill.

8.5 TRANSFER, STORAGE, AND HANDLING OPERATIONS

8.5.1 Models Documented in AP-42

Emission methods for the following models were taken from AP-42; they have been developed from the field data in the petroleum industry and should be applicable to TSDF:

- Container loading (from AP-42, Section 4.4)[52]
- Container cleaning (from AP-42, Section 4.8)[53]
- Stationary tank loading (from AP-42, Section 4.3)[54]

TABLE 8-24. MODEL INPUT PARAMETERS USED IN APPLICATION OF THE RTI LAND TREATMENT MODEL TO AN ACTIVE LANDFILL AT SITE 5[a]

Parameter	Value	Data source
L, total organic loading in soil	2.65×10^{-3} g/cm^3	Inferred from field data (solid sample analysis) assuming soil density = 2.3 g/cm^3
C_i, weight fraction of constituent i in organic phase	Xylene: 0.178 Methylene chloride: 8.48×10^{-4} Tetrachloroethylene: 1.37×10^{-3}	Computed from field data (solid sample analysis)
T, temperature of constituent vapor in soil	25 °C	Default value
l, depth of waste in landfill	229 cm (7.5 ft)	Default value
ϵ_T, total porosity of waste	0.50 (50%)	Default value
ϵ_a, air porosity of waste	0.25 (25%)	Default value
S_b, soil biomass concentration	0 g/cm^3	Default value
MW_{oil}, molecular weight of organic carrier liquid	150 g/g mol	Default value
t, time between soil sampling and air emission measurement	900 s (15 min)	Engineering judgment

[a] Landfill 10, General Organic Cell.[46,47]

TABLE 8-25. COMPARISON OF MEASURED AND PREDICTED EMISSION RATES FOR SITE 5 ACTIVE LANDFILL[a]

Chemical	Field data result, $\mu g/m^2 \cdot s$	Model prediction, $\mu g/m^2 \cdot s$
Xylene	32.8	440.0
Methylene chloride	0.734	14.0
Tetrachloroethylene	0.0111	4.9

[a] Landfill 10, General Organic Cell.[48,49]

TABLE 8-26. MODEL INPUT PARAMETERS USED IN APPLICATION OF THE RTI LAND TREATMENT MODEL TO AN ACTIVE LANDFILL AT SITE 8[50]

Parameter	Value	Source
L, total organic loading in soil	1.71×10^{-6} g/cm^3	Field data
C_i, weight fraction of VO_i in organic phase	Xylene: 0.012 1,1,1-TCE: 0.19 Tetrachloroethylene: 0.096	Computed from field data (solid sample analysis)
T, temperature of VO vapor in soil	25 °C[a]	Default value
l, depth of waste in landfill	229 cm (7.5 ft)	Default value
ϵ_T, total porosity of waste	0.50 (50%)[b]	Default value
ϵ_a, air porosity of waste	0.25 (25%)[b]	Default value
S_b, soil biomass concentration	0 g/cm^3	Default value
MW_{oil}, molecular weight of organic carrier liquid	150 g/g mol	Default value
t, time between soil sampling and air emission measurement	900 s (15 min)	Engineering judgment

[a] Soil surface temperatures at this site were reported at 26 to 36 °C. The model unit default value of 25 °C is applied to the constituent within the soil in this analysis.

[b] A single "porosity" value of 31.7 percent was reported for this site, based on one soil sample. Because this value is not defined explicitly, and may not be representative of typical waste in the landfill, the model unit default values of air porosity and total porosity were applied in this analysis.

TABLE 8-27. COMPARISON OF MEASURED AND PREDICTED EMISSION RATES FOR THE SITE 8 ACTIVE LANDFILL[51]

Chemical	Field data result, $\mu g/m^2 \cdot s$	Model prediction, $\mu g/m^2 \cdot s$
Total xylene	6.21	0.23
1,1,1-Trichloroethane	3.57	3.8
Tetrachloroethylene	6.31	1.9

- Stationary tank storage (from AP-42, Section 4.3).[55]

8.5.2 Fugitive Emissions

Fugitive emission sources have been studied extensively for the petroleum and Synthetic Organic Chemical Manufacturing Industries (SOCMI) facilities.[56] These SOCMI emission factors are assumed to be applicable to similar operations at TSDF.

8.5.3 Spillage

An ICF[57] study of truck transport to and from TSDF and truck emissions at TSDF terminals provided the information necessary to estimate spillage losses during TSDF and trucking operation. However, none of the reports listed in Appendix F of the BID contains field test data for comparison.

8.5.4 Open Dumpster Storage Emissions

No field data were available for comparison.

8.6 REFERENCES

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APPENDIX A

CHEMDAT6 USER'S GUIDE

APPENDIX A

CHEMDAT6 USER'S GUIDE

A.1 INTRODUCTION

CHEMDAT6 is a Lotus 1,2,3 spreadsheet that includes analytical models for estimating volatile organic (VO) compound emissions from treatment, storage, and disposal facility (TSDF) processes under user-specified input parameters. The available models include disposal impoundments, closed landfills, land treatment facilities, and aeration and nonaeration impoundment processes. Predicted emissions can be viewed on the screen or printed. A graphical presentation of the relationships between emission prediction and vapor pressure and between emission prediction and the partition coefficient is also available to the user. The resulting scatter diagrams can be printed via PrintGraph, another Lotus procedure.

VO emission models from hazardous waste TSDF were described in Sections 4.0, 5.0, 6.0, and 7.0 of this report. The emission rates from some TSDF can be estimated via CHEMDAT6. In this regard, Exhibit A-1 specifies the appropriate CHEMDAT6 model to estimate emissions from particular TSDF. For example, the nonaerated impoundment model in CHEMDAT6 can estimate emissions from storage impoundments. The CHEMDAT6 model for predicting emissions from treatment impoundments is the aerated impoundment model. Furthermore, the land treatment model in CHEMDAT6 can estimate emissions from land treatment soil, open landfills, and wastepiles. Emissions from an oil film surface in a land treatment facility or an oil film on a surface impoundment are predicted via the oil film model in CHEMDAT6. When a CHEMDAT6 model is not available to predict emissions, the reader must resort to the prediction equations in the previous sections of this report to estimate VO emissions from TSDF.

CHEMDAT6 calculates the fractions of waste constituents of interest that are distributed among the pathways (partition fractions) applicable to the facility under analysis. Estimated annual emissions from many of the

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TSDF are calculated by this spreadsheet. Otherwise, estimated annual emissions can be calculated offline by multiplying the throughput of the constituent of interest by the partition fraction.

The sixth version of the CHEMDAT spreadsheet contains several major operational modifications. In CHEMDAT6, the user can select a subset of target compounds for investigation. The user can also specify which TSDF processes are to be considered during a session. These two selections improve the efficiency of CHEMDAT6 relative to earlier versions by minimizing storage requirements as well as the actual loading and execution time.

Default input parameters in the accompanying CHEMDAT6 diskette demonstrate example calculations in Sections 4.0, 5.0, and 6.0 of this report. However, the user can readily change the input parameters to reflect different hazardous waste TSDF characteristics and then recalculate emissions under these modified conditions. The diskette with this user's guide is write-protected. It is suggested that a copy be used in estimating emissions. Furthermore, the list of compounds in CHEMDAT6 can be augmented by any of the 700 chemicals in Appendix D. Procedures for introducing additional compounds into CHEMDAT6 are described in Appendix D.

Instructions on the use of CHEMDAT6 appear in this appendix. (We have assumed throughout this appendix that the user has some minimal knowledge of Lotus 1,2,3.) CHEMDAT6 contains a data base of component-specific properties used to generate internally the inputs for the environmental fate models of waste disposal practices. This data base and model parameters are described in Section A.2. Section A.3 specifies how to get started in Lotus 1,2,3. Section A.4 details proper utilization and modification of CHEMDAT6 via the alternative command menu. The steps required to obtain a printout of the graphs are described in Section A.5. The referenced exhibits complete this appendix.

A.2 ANATOMY OF THE CHEMDAT6 SPREADSHEET

This section describes the structure of the CHEMDAT6 spreadsheet; a generalized layout of the spreadsheet appears in Attachment A. In general, rows 1 through 5 of this spreadsheet contain column labels or names. The compound-specific data base and calculation results appear in rows 14 through 74. The locations of model-specific input parameters are specified throughout Section A.2.3.

A.2.1 Data Base

The data base in the CHEMDAT6 spreadsheet is a matrix of component-specific properties or calculations. Sixty-one chemicals or compounds appear in rows 14 through 74 of the spreadsheet. These compounds are listed in Exhibit A-2.

Compound properties and model computational results appear in columns B through BU of the spreadsheet. For example, molecular weight appears in column D. Thus, each compound-specific data item has a unique cell address "cr" where c (alphabetic) represents the appropriate column and r (numeric) the row. Suppose data on toluene appear in row 16 of the CHEMDAT6 spreadsheet. Then, the molecular weight of toluene would appear in cell D16.

A.2.2 Column Labels

In general, column labels or names appear in rows 1 through 5 of the spreadsheet. Exhibit A-3 lists the column labels in CHEMDAT6.

A.2.3 Model Input Parameters and Predicted Emissions

Brief descriptions and locations of the CHEMDAT6 model-specific parameters are presented in the following subsections. Additionally, use of CHEMDAT6 is demonstrated via example calculations presented previously in this report. VO emissions estimated from CHEMDAT6 models are compared to the example calculation results.

Missing data in the CHEMDAT6 spreadsheet (e.g., vapor pressure for dioxin) frequently preclude estimating emission rates for the affected compound. In such cases, "ERR" is printed in place of the estimated emission. The user is encouraged to insert these missing data as values become available. The procedure for modifying input parameters is described in Section A.4.1.

A.2.3.1 Nonaerated Model. CHEMDAT6 nonaerated model input parameters are located in cells CO6 through CO15 of the spreadsheet and are illustrated in Exhibit A-4. (This and subsequent exhibits depict what the user will see on the computer screen.) The windspeed in meters/second is placed in CO6. CO7 contains the depth of the nonaerated impoundment (in meters). The surface area of the impoundment (in meters squared) and the flow rate (in cubic meters/second) appear in CO8 and CO9, respectively. The VO inlet concentration expressed in milligrams/liter is placed in CO10. Cell CO11 contains the sum of the organics (in milligrams/liter) entering the facility. Note that the VO inlet concentration in C010 should be less than the overall concentration of organics in C011. The maximum biorate in the TSDF (see equation 4.28), expressed in milligrams of organic matter/milligram of biotic matter/hour appears in C012. Because biodegradation is presumed to be nonexistent in a storage impoundment, the amount of active biomass (C013) has been set at zero. If the uniqueness of the TSDF permits biodegradation as a pathway and the user desires to consider its impact on emissions, C013 can be changed to reflect active biomass using standard Lotus procedures (see Section A.4.1). The input parameter, biomass solids in (C014), is appropriate for municipal facilities only. A good approximation of the biomass input for adsorption in municipal facilities is 1 percent of the flow. The ambient air temperature for the facility in degrees Celsius is placed in C015.

The nonaerated model input parameters in Exhibit A-4 have the same values as those used in the example calculation for storage impoundments in Section 4.2.3 where the compound of interest is benzene. The predicted emissions for benzene from CHEMDAT6 (see Exhibit A-4) are equivalent to those model results presented in the latter portion of Section 4.2.3. The predicted fraction of benzene that will be emitted to the air is calculated as 0.801. The estimated annual air emissions of benzene from the example nonaerated surface impoundment total 0.39 Mg. CHEMDAT6 model input parameters and results are printed using the PRINT option as discussed below in Section A.4.4.

In contrast, the example calculation in Section 4.3.3 considers biodegradation as a pathway. The amount of active biomass is 0.05 g/L; see Exhibit A-5. The remaining model input parameters are identical to those in Section 4.2.3. Almost 59 percent of the benzene is emitted to the air so that the annual emission rate is 0.29 Mg/yr.

A.2.3.2 Aerated Model. CHEMDAT6 parameters for the aerated impoundment model are located in column CO, rows 78-88, and column CS, rows 79-85 (see Exhibit A-6) The equations for estimating relative pathways include those for the quiescent surface of nonaerated systems, but these must be supplemented to account for a turbulent zone.

Because biodegradation is assumed to occur in aerated impoundments, the amount of active biomass (grams/liter) must be specified in C082. Cell C087 contains the fraction of the impoundment's surface area that is agitated. The submerged air flow (m^3/s) in C088 accommodates a mechanical air source located below the surface of the impoundment. Consequently, emissions from a diffused air flow-through system, i.e., one that emphasizes biodegradation, are estimated by placing an appropriate value in C088. The remaining input parameters in column CO are the same as those explained in the previous section.

The number of impellers is specified in CS79. The oxygen transfer rating of the aerator (pounds O_2/horsepower/hour) appears in CS80. The total power of the mechanical aeration system expressed in horsepower is placed in cell CS81. Cell CS82 contains the oxygen transfer correction factor (no units). The remaining parameter inputs include the water temperature (CS83) in degrees Celsius, the impeller diameter (CS84) in centimeters, and the impeller speed (CS85) in rads/second. If the impoundment's surface is not agitated (C087=0), the final seven model input parameters (CS79-CS85) are ignored in the emission calculations.

The aerated model input parameter values in Exhibit A-6 are the same as those used in the example for a mechanically aerated treatment impoundment discussed in Section 4.4.3. The compound of interest is benzene. CHEMDAT6 reproduces the materials balance results presented in Section 4.3.3.f; see Exhibit A-6. The predicted fraction of benzene that will be emitted to the air is 0.98. The estimated annual air emissions of benzene from such aerated impoundments are 0.97 Mg.

Emission results for the activated sludge unit in Section 4.4.4 and the diffused air activated sludge unit in Section 4.6.3 are also available from the CHEMDAT6 aerated model. See Exhibits A-7 and A-8, respectively, for the model input parameters, the materials balance results, and the annual air emission rate.

A.2.3.3 Land Treatment Model. The CHEMDAT6 land treatment model can predict emissions from land treatment soil, open landfills, and wastepiles. A general description of the land treatment model parameters is followed by specific guidelines for each application.

The land treatment model parameters for CHEMDAT6 are located in cells CV7 to CV18 as illustrated in Exhibit A-9. The oil loading must be obtained from the site operator or manually calculated offline as indicated in the report. It then is entered in CV7. The weight concentration of the VO (ppm by weight) (see CV8) is in the oil phase (for a two-phased liquid), in the water (for a dilute aqueous liquid), or in the liquid (for an organic liquid waste). The depth (CV9) is the depth of tilling in the land treatment facility in centimeters. The total porosity and the air porosity appear in CV10 and CV11, respectively. CV12 contains the average molecular weight of oil. In cell CV13, the value "1" is entered if the waste liquid is a dilute aqueous solution or a "0" is entered for an (Raoult's law) organic waste or a two-phase (water + organic liquid) waste model. An intermediate time period over which emissions are to be calculated is specified in CV14 in units of days. Cell CV15 is an indicator for biological activity in the TSDF. When the user selects the land treatment model to predict emissions from land treatment soil, this flag is automatically set to 1. When the land treatment model is used to predict emissions from open landfills or wastepiles, biodegradation is assumed not to occur, and this indicator is automatically set to zero. The user may change this value if biodegradation is to be considered in the open landfill or wastepile. The remaining three parameters have been described previously.

The values of these parameters in Exhibit A-9 estimate relative emissions from land treatment soil for benzene under the scenario detailed in Section 5.2.6.1. The estimated emissions for benzene presented in this section correspond to the CHEMDAT6 predictions in Exhibit A-9. Because an intermediate time period of 365.25 days was specified in CV14, the intermediate time emission fractions reflect annual estimates. The predicted annual fraction of benzene that will be emitted to the air is calculated as 0.90. This is equivalent to the example calculation result for land treatment facilities in Section 5.2.6.1.g. The long-term emission fraction for this example is equal to the intermediate result. Annual air emissions of benzene from the land treatment soil can be estimated from these results as follows:

Calculation

From Section 5.2.6.1:

Annual throughput: 1,800 Mg
Oil content of waste: 10 percent
Benzene concentration in oil: 2,000 ppm

$E = 0.903 \times 1{,}800 \text{ Mg} \times 0.10 \times 0.002 = 0.33 \text{ Mg/yr}$.

Benzene emission from the land treatment facility is 0.33 Mg/yr.

Short-term emission results for the land treatment facility are also available from CHEMDAT6. Exhibit A-10 contains the estimated emission rates for benzene at 1/4, 1, 4, 12 and 24 hours after application to the land treatment soil.

Different tilling frequencies can also be accommodated by using the CHEMDAT6 land treatment model to predict emissions for each time period defined by the tilling frequencies. This approach additionally requires that initial weight concentration of the VO (CV8) for each time period be adjusted for the estimated mass of the VO emitted or biodegraded during the previous time period. For each run of the model, the time period (in days) over which emissions are to be calculated is placed in CV14.

As indicated previously, the CHEMDAT6 land treatment model can be used to estimate emissions from open landfills. Exhibit A-11 contains the CHEMDAT6 land treatment model parameters and emission results that correspond to the example calculation in Section 6.4.3 for predicting the emission fraction of chloroform from open landfills. Because biodegradation is presumed not to occur in an open landfill, CV15 has been set to zero.

One year post-application, the fraction of chloroform lost to the atmosphere from open landfills is 0.053 from both CHEMDAT6 and the example calculation in Section 6.4.3.d. The following calculation demonstrates how to convert this emission fraction into an annual emission rate for an open landfill.

Calculation

From Section 6.4.3:

Landfill depth: 229 cm
Landfill area: $1.42 \times 10^8 \text{ cm}^2$

Loading: 0.46 g/cm^3

Weight fraction of chloroform in oil: 0.5

$E = 229 \text{ cm} \times 1.42 \times 10^8 \text{ cm}^2 \times 0.46 \text{ g/cm}^3 \times 0.5 \times 1 \text{ Mg}/10^6 \text{ g} \times 0.053$

$= 4.0 \times 10^2$ Mg/yr.

Estimates of long-term emission and biological fractions from open landfills for chloroform are 1.0 and 0.0, respectively.

Finally, emissions from wastepiles also can be estimated via the CHEMDAT6 land treatment model under the restriction that the time parameter (CV14) must be less than or equal to the life of the wastepile. In the wastepile scenario discussed in Section 6.4.2.2, the retention time is 2.6 days. The user can estimate the emission fraction for any time period less than or equal to 2.6 days via CHEMDAT6 by placing the selected time period (expressed in days) in CV14. The average height of the wastepile, 100 cm, is placed in CV9. The remaining CHEMDAT6 input parameters would be identical to those in Exhibit A-8. The emission rate for the time period specified in CV14 is calculated from the resultant emission fraction as for the open landfill. Multiply this value by 140, the estimated number of turnovers per year, to obtain the annual emission rate of chloroform for the wastepile. The user is reminded that, for open landfills and wastepiles, the biomass concentration in the land treatment model defaults to zero (CV15).

A.2.3.4 Disposal Impoundment Model. CHEMDAT6 disposal impoundment model input parameters are located in C046 through C056 of the spreadsheet. Please refer to Exhibit A-12. The concentration of VO (C051) is the initial concentration in the waste expressed in milligrams/liter. The adsorbing biomass concentration (in C050) is the concentration available to remove the VO. This and the active biomass concentration (grams/liter in C049) are set to zero when adsorption and biodegradation are assumed to be nonexistent in a disposal impoundment. The remaining input parameters were previously defined.

The parameters specified in Exhibit A-12 reflect the example calculation for benzene emissions from a disposal impoundment described in Section 4.4.3. The CHEMDAT6 emission results also shown in this exhibit suggest that 75 percent of the benzene in the disposal impoundment will have been emitted to the air in the specified period of 6 months. Section 4.4.3 contains the same fractional result. With two turnovers per year, the corresponding emission rate is 0.24 Mg/yr.

The CHEMDAT6 disposal impoundment model can also estimate emissions from a diffused air system. This modification is achieved by defining a positive (nonzero) submerged air flow (m^3/second) in C055. If the user wishes to consider biodegradation as a pathway in the diffused air system, the concentration of active biomass (g/L) should be placed in C049.

A.2.3.5 Closed Landfill Model. Cells CV30 through CV52 in the CHEMDAT6 spreadsheet contain the closed landfill model input parameters; see Exhibit A-13. The user must first select the appropriate model. The options include the aqueous model (CV50=1) and the (Raoult's law) two-phased or organic liquid model (CV50=0). Additional CHEMDAT6 specifications are required for each of these models.

With the dilute aqueous model:

- The weight fraction oil (CV41) is set at zero (consequently, the sum of weight fraction water (CV42) and weight fraction VO (CV43) must be one).
- MW-liquid (CV52) and rho-liquid (CV51) are used in the estimation procedure. Default values of 18 g/g mol and 1 g/cm^3, respectively, appear in the software as information to the user. These values cannot be changed.
- mwt oil (CV45) does not contribute to the emission prediction.
- Liquid in waste (CV44) is set at 1 g/cm^3 in accordance with dilute aqueous waste.

With the (Raoult's law) two-phased model:

- The values of MW-liquid (CV52) and rho-liquid (CV51) are ignored in the emission estimation process.

Finally, the closed landfill model can accommodate biodegradation. The input parameter CC/GVOC CONV (CV48) is the amount of gas produced in cubic centimeters per gram of VO biodegraded and is only applicable when biodegradation is considered a pathway. The user may wish to change the given representative value of CC/GVOC CONV to investigate other scenarios. The amount of active biomass (g/cc) is placed in CV49. The emissions then are augmented by those resulting from this additional pathway. Please note that the gas conversion input is ignored if biodegratation is presumed not to occur (i.e., when biomass in CV49 is set to zero). The remaining closed landfill model parameters are self-explanatory.

The values of the closed landfill model parameters in Exhibit A-13 correspond to those in the example calculations of chloroform emissions from a closed land-fill (see Section 6.2.3). A two-phased model was used, and both the instantaneous emission rate after 1 year and the average emission rate in the first year were equivalent (13.0 Mg/yr of chloroform is the value for both rates from the sample calculations) to the estimated emission values from the CHEMDAT6 landfill model as shown in Exhibit A-13.

A.2.3.6 Oil Film Model. The CHEMDAT6 oil film model predicts emissions from an oil film surface impoundment or from an oil layer on land treatment soil. Input parameters for the oil film model are located in cells CV69 to CV78; see Exhibit A-14. Depth in meters (CV70) refers to the oil film thickness measured in meters. Area (CV71) is the surface area of the facility in square meters. Flow (CV72) is the rate of flow through a surface impoundment and, consequently, is not applicable when predicting emissions from an oil layer on land treatment soil. When there is no flow, set CV72 to zero and enter the number of months for disposal in CV77. This latter input is needed to calculate residence time.

The input parameters specified in Exhibit A-14 reflect the example calculation for butanol-1 emissions from an oil layer on the soil surface of a land treatment site as described in Section 5.2.3.3. This exhibit shows the equivalent CHEMDAT6 emission result.

A.2.4 Miscellaneous

References for various compound properties appear in cells P77 through P85 and V83 through V84.

A.3 GETTING STARTED IN LOTUS 1,2,3

The applications program, Lotus 1,2,3, should be installed on the computer system for use. Place the diskette containing CHEMDAT6 in drive B.

Access the 1,2,3 mode of operation in Lotus. A skeleton of a spreadsheet will appear on the screen, and the message READY will appear in the upper right corner of the screen. (Consider this and other messages as road signs that guide you through CHEMDAT6.) To retrieve CHEMDAT6, press the following sequence of keys, i.e., those keys that appear between brackets { }:

{/} {F} {R} .

Note that {/} calls the active command mode. (The active command mode is indicated by the message MENU in the upper right corner of the screen.) The F represents file and the R represents retrieve. In other words, these are the commands to retrieve a file. We indicate the file to retrieve by typing the drive label, followed by a colon, followed by CHEMDAT6,

{B:CHEMDAT6} ,

and then pressing {RETURN}.

An equivalent approach is to position the cursor over CHEMDAT6, which appears below the command line, and then press {RETURN}. The cursor controls (keys with arrows on top, i.e., ↑, ↓, —>, and <—) position the cursor. After CHEMDAT6 loads for a minute or two (note the message WAIT flashing in the upper right corner of the screen), the user will be in the alternative command menu developed specifically for CHEMDAT6. The message CMD in the upper right corner of the screen indicates that the alternative command menu is active. A discussion of this menu follows.

A.4 ALTERNATIVE COMMAND MENU

The alternative command menu is a menu-driven set of instructions specific to CHEMDAT6. Choose an option (DATA-FORMS, VIEW, SORT, PRINT, SELECT, HELP, or QUIT) by positioning the cursor over the selection and pressing {RETURN}. Alternatively, the first letter or set of letters that uniquely identify the selection can be entered: e.g., {P} can be pressed to choose the PRINT option. Alternative command menu options and suboptions are listed in Exhibit A-15; please study this guide carefully. If you get lost after accessing the alternative command of CHEMDAT6, the first level of options (DATA-FORMS, VIEW, etc.) can be accessed via {ALT M}. "ALT M" stands for the alternative command menu.

A.4.1 DATA-FORMS Option

The DATA-FORMS option in the alternative command menu is the crux of this software package. It is the vehicle by which the user can change model input parameters in CHEMDAT6.

Once the user has specified {DATA-FORMS} and has selected the desired model, the corresponding input parameters will appear highlighted on the computer screen. Move the cursor to the cell location containing the model input parameter to be modified. After the proper cell has been located in the spreadsheet with the cursor, type the new input parameter, then press {RETURN}. The new input parameter will appear on the screen. At this point, the message CALC will appear in the lower right side of the screen indicating that the model predictions must be recalculated to reflect the new input parameter. Once all the input parameters have been modified, press {ESC} to exit the data base and then {F9} to recalculate the emission predictions under the new input parameters. The WAIT message will flash as the model predictions are recalculated. The CALC message will disappear once the model predictions have been revised. The user must perform this latter step so that the emission results will reflect the modified input parameters. Furthermore, this revised spreadsheet must be saved if updated graphs are desired.

To save the revised spreadsheet, access the active command mode (press {ALT M} {Q}). Then type

{/} {F} {S} {CHEMDAT6} {R} ,

where F represents file, S represents save, and R represents replace. Consequently, the old version of the CHEMDAT6 spreadsheet is replaced by the new, modified version.

Finally, the DEFAULT suboption for DATA-ENTRY is used to replace model input parameters with the default values, i.e., those values corresponding to example calculations described in Section A.2.3. The model default values for nonaerated and aerated wastewater treatment, land treatment soil, open landfills, disposal impoundments, and closed landfills appear in Exhibits A-5, A-6, A-9, A-11, A-12, and A-13, respectively. After input parameters are replaced with default values, remember to recalculate model predictions.

A.4.2 VIEW Option

A.4.2.1 Viewing Model Emission Results. The VIEW option enables the user to view on the computer screen emission results from disposal impoundments, land treatment facilities, open landfills/wastepiles, closed landfills, and nonaerated and aerated models. Exhibit A-15 describes the options and suboptions available. To exit the model results, press {ALT M}.

A.4.2.2 Viewing Graphs. The user is able to view graphs on the computer screen by pressing {VIEW} {GRAPH} and then selecting the desired model. The user must exit from this procedure via {QUIT} in order to reformat the spreadsheet.

A.4.3 SORT Option

This option in the alternative command menu enables the user to rearrange the order of the compounds in the CHEMDAT6 spreadsheet. Suboptions include sorting by biorate, selected compound, alphabetically, by compound type (class), and by vapor pressure. Model predictions must be recalculated after sorting.

The {SELECT} suboption under {SORT} is a very powerful feature of CHEMDAT6. Analogous to a "cut and paste" procedure, {SORT} {SELECT} enables the user to select a subset of the 61 compounds for entry into the CHEMDAT6 spreadsheet. Model calculations are only performed for the selected compounds, which improves the performance of the spreadsheet. Consequently, emission results are limited to the selected compounds. This {SELECT} {SORT} option was employed to choose the compound of interest, benzene, in previous exhibits.

Two approaches are available for selecting compounds. To select a set of chemicals, use a "1" to flag those compounds of interest. Those compounds preceded with a "0" will be ignored. The user may also order the selected compounds so that compound-specific emission results are printed in a desired sequence. If there are n compounds of interest, place an integer from 1 to n in front of each compound. Once {ALT} {Z} is typed, CHEMDAT6 will rearrange the compounds in descending order according to this integer. As before, emission results will not be estimated for those compounds preceded by a "0".

A.4.4 PRINT Option

The PRINT option allows the user to obtain a hard copy of model-specific emission results (via the suboptions LAND-TREAT, DISPOSAL, AERATED, LANDFILL, and NON-AERATED) and the corresponding set of input parameters as well as data summaries (via the DATA suboption). The data summaries include biorate data (refer to columns P through X in Exhibit A-3), land treatment data (see columns AM and AN in Exhibit A-3), and selected data tables (see columns F, G, H, and I in Exhibit A-3) that are printed via the commands {PRINT} {DATA} {BIORATE}, {PRINT} {DATA} {LANDTREAT}, or {PRINT} {DATA} {DATA}, respectively. Examples of printed model input parameters and emission results appear in Exhibits A-4 through A-14.

The PRINT option has another important function: it enables the user to store the graph file on the diskette. Enter the commands {PRINT} {GRAPH} followed by the selected model. This procedure is required to obtain a hard copy of the model-specific graph. Further details are provided in Section A.5.

A.4.5 HELP Option

The HELP option provides the user with information regarding the proper application and various assumptions of the specific models in CHEMDAT6. A general help screen is also available.

A.4.6 SELECT Option

The SELECT option in the main menu, another "cut and paste" feature of CHEMDAT6, allows the user to activate only a subset of the TSDF models for entry into the spreadsheet. Models are selected through the 0-1 (off-on) flag system described prevously. Note that, if the user attempts to use a model that is not active, error messages will be printed instead of model emission results.

A.4.7 QUIT Option

The active command mode can be accessed from the alternative command menu by locating the cursor over {QUIT} and pressing {RETURN}. In this mode, all the features of Lotus 1,2,3 are available by pressing {/}.

A.5 PRINTING A GRAPH

A.5.1 Graph Selection

Two types of graphs are available in CHEMDAT6. The first is a plot of emission prediction versus the partition coefficient; the second is a plot of emission prediction versus vapor pressure. Both graphs are available for all models except the oil film. Select a graph in the active command mode via

{/} {G} {N} {U} ,

where G represents graph, N represents new, and U represents use. (Recall that you can also position the cursor over the desired option and press {RETURN}.) Now select the desired graph. GRAPH-PC is the plot of emission prediction versus the partition coefficient, and GRAPH-VP is the plot of emission prediction versus vapor pressure. You can ignore the plot that appears on your screen. To return to the alternative command menu, press {ESC}, {QUIT}, {ALT M}.

A.5.2 Storing the Graph File

The sequence {PRINT} {GRAPH} followed by selection of the desired model will create the plot chosen via Section A.5.1 for the selected model and simultaneously store it in a specific file on the diskette (see Section A.4.1). CHEMDAT6 will store only one plot for each model. Furthermore, it stores the most recently created plot. Consequently, the user must first create the plot for which he wants a hard copy using the procedures described in this and the previous section.

A.5.3 The Hard Copy

To obtain a hard copy of a plot, access the active command mode; follow the commands to exit Lotus 1,2,3; and then access Lotus {PRINTGRAPH}. Once in this mode, {SELECT} plots for printing using the space bar to flag (#) the desired plots. The most recently created plot for closed landfill emissions is Q1; for land treatment emissions, Q2; for nonaerated process emissions, Q3; for aerated process emissions, Q4; and for disposal impoundment emissions, Q5. Press {RETURN} and then {Go} to print the selected plots.

TSDF (Section)	CHEMDAT6 Model
SURFACE IMPOUNDMENTS AND OPEN TANKS	
Storage impoundments (4.2)	Nonaerated impoundment
Treatment impoundments, mechanically aerated systems (4.3)	Aerated impoundment
Disposal impoundments (4.4)	Disposal impoundment
Diffused air systems (4.5)	Disposal or aerated impoundments
Oil film surfaces (4.6)	Oil film
LAND TREATMENT	
Land treatment soil (5.2)	Land treatment
Waste application (5.2)	NA
Oil film surface (5.2)	Oil film
LANDFILLS AND WASTEPILES	
Closed landfills (6.2)	Closed landfill
Fixation pits (6.3)	NA
Open landfills (6.4)	Land treatment (modified)
Wastepiles (6.4)	Land treatment (modified)
TRANSFER, STORAGE, AND HANDLING OPERATIONS	
Container loading (7.2)	NA
Container storage (7.3)	NA
Container cleaning (7.4)	NA
Stationary tank loading (7.5)	NA
Stationary tank storage (7.6)	NA
Spills (7.7)	NA
Fugitive emissions (7.8)	NA
Vacuum truck loading (7.9)	NA

NA = Not available in CHEMDAT6.

EXHIBIT A-1. RELATIONSHIP BETWEEN HAZARDOUS WASTE TSDF AND CHEMDAT6 MODELS

COMPOUND NAME	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	H LAW CONST. (atm-m3/mol)	DIFF. WATER (cm2/sec)
ACETALDEHYDE	44.0	0.79	760	9.50E-05	1.41E-05
ACETONE	58.0	0.79	266	2.50E-05	1.14E-05
ACROLEIN	56.1	0.84	244.2	5.66E-05	1.22E-05
ACRYLONITRILE	53.1	0.81	114	8.80E-05	1.34E-05
ALLYL ALCOHOL	58.1	0.85	23.3	1.80E-03	1.14E-05
BENZENE	78.1	0.87	95.2	5.50E-03	9.80E-06
BENZYL CHLORIDE	126.6	1.10	1.21	6.10E-03	7.80E-06
BUTANOL-1	74.1	0.81	6.5	8.90E-06	9.30E-06
CARBON DISULFIDE	76.1	1.26	366	1.68E-02	1.00E-05
CARBON TETRACHLORIDE	153.8	1.59	113	3.00E-02	8.80E-06
CHLOROBENZENE	112.6	1.11	11.8	3.93E-03	8.70E-06
CHLOROFORM	119.4	1.49	208	3.39E-03	1.00E-05
CHLOROPRENE	88.5	0.958	273	0.331	1.00E-05
CRESOL(-m)	108.1	1.03	0.08	4.43E-07	1.00E-05
CRESOL(-o)	108.1	1.05	0.24	2.60E-06	8.30E-06
CRESOL(-p)	108.1	1.03	0.11	4.43E-07	1.00E-05
CRESOLS	108.1	1.03	0.143	2.60E-06	1.00E-05
CRESYLIC ACID	108.0	1.05	0.3	1.70E-06	8.30E-06
CUMENE (isopropylbenzene)	120.2	0.86	4.6	1.46E-02	7.10E-06
CYCLOHEXANONE	98.2	0.95	4.8	4.13E-06	8.62E-06
DICHLOROBENZENE(1,2) (-o)	147.0	1.31	1.5	1.94E-03	7.90E-06
DICHLOROBENZENE(1,4) (-p)	147.0	1.29	1.2	1.60E-03	7.90E-06
DICHLOROETHANE(1,2)	99.0	1.26	80	1.20E-03	9.90E-06
DIMETHYL NITROSAMINE	74.08	1.005			1.00E-05
DIOXIN	250				1.00E-05
EPICHLOROHYDRIN	92.5	1.18	17	3.23E-05	9.80E-06
ETHYLACETATE	88.1	0.90	100	1.28E-04	9.66E-06
ETHYLBENZENE	106.2	0.87	10	6.44E-03	7.80E-06
ETHYLENEOXIDE	44.0	0.87	1250	1.42E-04	1.00E-05
ETHYLETHER	74.1	0.71	520	6.80E-04	9.30E-06
FORMALDEHYDE	30.0	0.00	3500	5.76E-05	1.98E-05
FREONS	120.92	1.486	5000	4.01E-01	1.00E-05
HEXACHLOROBUTADIENE	260.8	1.67	0.15	2.56E-02	6.16E-06
HEXACHLOROCYCLOPENTADIENE	272.8	1.71	0.081	1.60E-02	6.16E-06
ISOBUTYL ALCOHOL	74.0	0.79	10	2.20E-06	9.30E-06
MALEIC ANHYDRIDE	98.1	0.93	0.0001	4.00E-08	1.11E-05
METHANOL	32.0	0.79	114	2.70E-06	1.64E-05
METHYL ACETATE	74.1	0.92	235	1.15E-02	1.00E-05
METHYL ETHYL KETONE	72.1	0.82	100	4.35E-05	9.80E-06
METHYL ISOBUTYL KETONE	100.2	0.80	15.7	4.95E-05	7.80E-06
METHYLENE CHLORIDE	85.0	1.34	438	3.19E-03	1.17E-05
METHYLNAPHTHALENE (1)	142.2				
NAPHTHALENE	128.2	1.14	0.23	1.18E-03	7.50E-06
NITROBENZENE	123.1	1.20	0.3	1.31E-05	8.60E-06
NITROSOMORPHOLINE	116.14				1.00E-05
PHENOL	94.1	1.07	0.341	4.54E-07	9.10E-06
PHOSGENE	98.9	1.39	1394	1.71E-01	1.12E-05
PHTHALIC ANHYDRIDE	148.1	1.33	0.0015	9.00E-07	8.60E-06
POLYCHLORINATED BIPHENYLS	290	1.45		2.00E-04	1.00E-05
PROPYLENE OXIDE	58.1	0.83	524.5	1.34E-03	1.00E-05
PYRIDINE	79.1	0.98	20	2.36E-05	7.60E-06
TETRACHLOROETHANE(1,1,2,2)	168.0	1.59	6.5	3.80E-04	7.90E-06
TETRACHLOROETHLYENE	165.83	1.624	19	2.90E-02	8.20E-06
TOLUENE	92.4	0.87	30	6.68E-03	8.60E-06
TRICHLORO(1,1,2)TRIFLUOROETHANE(1,2,2)	187.38	1.58	300	4.35E-01	8.20E-06
TRICHLOROETHANE(1,1,1)	133.4	1.33	123	4.92E-03	8.80E-06
TRICHLOROETHYLENE	131.4	1.40	75	9.10E-03	9.10E-06
TRICHLOROFLUOROMETHANE	137.4	1.49	796	5.83E-02	9.70E-06
VINYL CHLORIDE	62.5	0.91	2660	8.60E-02	1.23E-05
VINYLIDENE CHLORIDE	97.0	1.21	591	1.90E-01	1.04E-05
XYLENE(-o)	106.2	0.88	7	5.27E-03	1.00E-05

EXHIBIT A-2. ALPHABETICAL LIST OF COMPOUNDS IN CHEMDAT6

COMPOUND NAME	DIFF. AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C
ACETALDEHYDE	1.24E-01	20.8	8.005	1600.017	291.809
ACETONE	1.24E-01	56.2	7.117	1210.595	229.664
ACROLEIN	1.05E-01	53.0	2.387833		
ACRYLONITRILE	1.22E-01	77.4	7.038	1232.53	222.47
ALLYL ALCOHOL	2.64E-01	97.0	1.367406		
BENZENE	8.80E-02	80.1	6.905	1211.033	220.79
BENZYL CHLORIDE	7.50E-02	179.4	0.082788		
BUTANOL-1	8.00E-02	117.7	7.476	1362.39	178.77
CARBON DISULFIDE	1.04E-01	46.3	6.942	1169.11	241.59
CARBON TETRACHLORIDE	7.80E-02	76.8	6.9339	1242.43	230
CHLOROBENZENE	7.30E-02	132.0	6.978	1431.05	217.55
CHLOROFORM	1.04E-01	61.2	6.493	929.44	196.03
CHLOROPRENE	1.04E-01	59.4	6.161	783.45	179.7
CRESOL(-m)	7.40E-02	202.0	7.508	1856.36	199.07
CRESOL(-o)	7.40E-02	190.8	6.911	1435.5	165.16
CRESOL(-p)	7.40E-02	203.0	7.035	1511.08	161.85
CRESOLS	7.40E-02	195	-0.84469		
CRESYLIC ACID	7.40E-02	235.0	-0.52289		
CUMENE (isopropylbenzene)	6.50E-02	153.0	6.963	1460.793	207.78
CYCLOHEXANONE	7.84E-02	157.0	0.681266		
DICHLOROBENZENE(1,2) (-o)	6.90E-02	179.0	0.176097		
DICHLOROBENZENE(1,4) (-p)	6.90E-02	173.4	0.079184		
DICHLOROETHANE(1,2)	1.04E-01	83.4	7.025	1272.3	222.9
DIMETHYL NITROSAMINE	1.04E-01	153			
DIOXIN	1.04E-01				
EPICHLOROHYDRIN	8.60E-02	117.0	1.230494		
ETHYLACETATE	7.32E-02	77.0	7.101	1244.95	217.88
ETHYLBENZENE	7.50E-02	136.2	6.975	1424.255	213.21
ETHYLENEOXIDE	1.04E-01	10.7	7.128	1054.54	237.76
ETHYLETHER	7.40E-02	34.5	6.92	1064.07	228.8
FORMALDEHYDE	7.40E-02	-14.0	7.195	970.6	244.1
FREONS	1.04E-01	-29.8	3.699106		
HEXACHLOROBUTADIENE	5.61E-02	215.0	-0.82393		
HEXACHLOROCYCLOPENTADIENE	5.61E-02	234.0	-1.09155		
ISOBUTYL ALCOHOL	8.60E-02	107.9	1.000036		
MALEIC ANHYDRIDE	9.50E-02	200.0	-4.00014		
METHANOL	1.50E-01	65.0	7.897	1474.08	229.13
METHYL ACETATE	1.04E-01	54.0	7.065	1157.63	219.73
METHYL ETHYL KETONE	8.08E-02	79.6	6.97421	1209.6	216
METHYL ISOBUTYL KETONE	7.50E-02	115.8	6.672	1168.4	191.9
METHYLENE CHLORIDE	1.0[illegible]-01	39.8	7.409	1325.9	252.6
METHYLNAPHTHALENE (1)					
NAPHTHALENE	5.90E-02	218.0	7.01	1733.71	201.86
NITROBENZENE	7.60E-02	210.8	7.115	1746.6	201.8
NITROSOMORPHOLINE	5.90E-02	225			
PHENOL	8.20E-02	182.0	7.133	1516.79	174.95
PHOSGENE	1.08E-01	8.2	6.842	941.25	230
PHTHALIC ANHYDRIDE	7.10E-02	284.0	8.022	2868.5	0
POLYCHLORINATED BIPHENYLS	1.04E-01				
PROPYLENE OXIDE	1.04E-01	33.9	2.719846		
PYRIDINE	9.10E-02	115.5	7.041	1373.8	214.98
TETRACHLOROETHANE(1,1,2,2)	7.10E-02	146.2	6.631	1228.1	179.9
TETRACHLOROETHLYENE	7.20E-02	121.4	6.976	1386.92	217.53
TOLUENE	8.70E-02	110.7	6.954	1344.8	219.48
TRICHLORO(1,1,2)TRIFLUOROETHANE(1,2,2)	7.80E-02	48.0	6.88	1099.9	227.5
TRICHLOROETHANE(1,1,1)	7.80E-02	75.0	8.643	2136.6	302.8
TRICHLOROETHYLENE	7.90E-02	87.0	6.518	1018.6	192.7
TRICHLOROFLUOROMETHANE	8.70E-02	23.8	6.884	1043.004	236.88
VINYL CHLORIDE	1.06E-01	-13.9	3.425008		
VINYLIDENE CHLORIDE	9.00E-02	31.9	6.972	1099.4	237.2
XYLENE(-o)	8.70E-02	144.4	6.998	1474.679	213.69

EXHIBIT A-2 (continued)

COMPOUND NAME	K (Y/X)	BIORATE mg VO per g biomass-hr
ACETALDEHYDE	5.277725	82.42
ACETONE	1.388875	14.55
ACROLEIN	3.144413	7.80
ACRYLONITRILE	4.88884	44.30
ALLYL ALCOHOL	99.999	0.00
BENZENE	305.5525	19.00
BENZYL CHLORIDE	338.8855	17.75
BUTANOL-1	0.494439	32.43
CARBON DISULFIDE	933.324	0.00
CARBON TETRACHLORIDE	1666.65	0.00
CHLOROBENZENE	218.3311	1.46
CHLOROFORM	188.3314	2.94
CHLOROPRENE	18388.70	0.00
CRESOL(-m)	0.024610	23.21
CRESOL(-o)	0.144443	22.78
CRESOL(-p)	0.024610	23.21
CRESOLS	0.144443	23.21
CRESYLIC ACID	0.094443	15.00
CUMENE (isopropylbenzene)	811.103	0.00
CYCLOHEXANONE	0.229608	11.49
DICHLOROBENZENE(1,2) (-o)	107.7767	10.00
DICHLOROBENZENE(1,4) (-p)	88.888	0.00
DICHLOROETHANE(1,2)	66.666	32.00
DIMETHYL NITROSAMINE	0	0.00
DIOXIN	0	0.00
EPICHLOROHYDRIN	1.794426	0.00
ETHYLACETATE	7.11104	17.58
ETHYLBENZENE	357.7742	46.38
ETHYLENEOXIDE	7.88881	0.00
ETHYLETHER	37.7774	0.77
FORMALDEHYDE	3.199968	29.91
FREONS	22277.55	0.00
HEXACHLOROBUTADIENE	1422.208	0.00
HEXACHLOROCYCLOPENTADIENE	888.88	0.00
ISOBUTYL ALCOHOL	0.122221	21.24
MALEIC ANHYDRIDE	0.002222	4.08
METHANOL	0.149998	12.00
METHYL ACETATE	638.8825	19.87
METHYL ETHYL KETONE	2.416642	73.77
METHYL ISOBUTYL KETONE	2.749972	0.74
METHYLENE CHLORIDE	177.2204	22.00
METHYLNAPHTHALENE (1)		24.03
NAPHTHALENE	65.5549	42.47
NITROBENZENE	0.727770	6.97
NITROSOMORPHOLINE	0	0.00
PHENOL	0.025221	33.61
PHOSGENE	9499.905	0.00
PHTHALIC ANHYDRIDE	0.049999	0.00
POLYCHLORINATED BIPHENYLS	11.111	0.00
PROPYLENE OXIDE	74.4437	0.00
PYRIDINE	1.311098	35.03
TETRACHLOROETHANE(1,1,2,2)	21.1109	0.00
TETRACHLOROETHLYENE	1611.095	0.00
TOLUENE	371.1074	73.48
TRICHLORO(1,1,2)TRIFLUOROETHANE(1,2,2)	24166.42	0.00
TRICHLOROETHANE(1,1,1)	273.1065	0.00
TRICHLOROETHYLENE	505.5505	0.00
TRICHLOROFLUOROMETHANE	3238.856	0.00
VINYL CHLORIDE	4777.73	0.00
VINYLIDENE CHLORIDE	10555.45	0.00
XYLENE(-o)	292.7748	40.79

EXHIBIT A-2 (continued)

Column	Column label [explanation]
B	COMPOUND NAME
C	COMPOUND TYPE
D	M.W. [molecular weight]
E	DENSITY (g/cc)
F	VAP.PRESS. (mmHg) [vapor pressure at 25 °C]
G	H LAW CONST (atm•m^3/mol) [Henry's law constant]
H	DIFF. WAT (cm^2/s) [diffusion coefficient in water]
I	DIFF. AIR (cm^2/s) [diffusion coefficient in air]
J	BOILING POINT (°C)
K	VAPOR PRESSURE COEFFICIENT - A
L	VAPOR PRESSURE COEFFICIENT - B
M	VAPOR PRESSURE COEFFICIENT - C
N	K(X/Y) [Henry's law coefficient, mol fraction]
O	LAND-TREATMENT BIORATE (DAY^{-1})
P	LOG OCT/WATER PARTITION
Q	BOD/COD RATIO
R	THOD (mg THOD/mg)
S	BIORATE (mg COD/g/h)
T	[reference for biorate data - see P78 through P85]
U	BIORATE (mg VO/g/h)

EXHIBIT A-3. LIST OF COLUMN LABELS IN CHEMDAT6

Column	Column label [explanation]	
V	PHOTOLY. (s^{-1}) [rate of photolysis]	
W	HYDROL. (s^{-1}) [rate of hydrolysis]	
X	ADS. (m^3/kg) [adsorption]	
Y	DISPOSAL IMPOUNDMENT - total fraction removed	
Z	OIL FILM - emissions fraction	
AA	[working column]	
AB	[working column]	
AC	[working column]	
AD	K_s (g/cm^3 per g/cm^3) [partition factor, VO into sludge]	
AE	Biorate (s^{-1})	NON-AERATED
AF	K_o ($g\ mol/cm^2$-s) = [overall mass transfer coefficient (m/s)] x 5.56	↓
AG	SUM RATES [sum of the various rate processes]	↓
AH	correl. conc. (mg/L) [correlation concentration]	
AI	biorate (s^{-1})	AERATED
AJ	K_o ($g\ mol/cm^2$-s) = [overall mass transfer coefficient (m/s)] x 5.56	↓
AK	SUM RATES [sum of various rate processes]	
AL	ADS. COEF. (VAP/SOL) [adsorption coefficient]	
AM	BIO RATES ($1/tb\ s^{-1}$) [biological rates]	
AN	DECAY PARAMETER	
AO	EMISS. FRACTION [emission fraction for specified period]	CLOSED LANDFILL
AP	BIOL. FRACTION [biological removal fraction for specified period]	↓
AQ	AVERAGE EMISSION RATE (Mg/specified time period)	↓

EXHIBIT A-3. (continued)

Column	Column label [explanation]	
AR	INSTANTANEOUS EMISSION RATE (Mg/specified time period)	LAND TREATMENT
AS	EMISS. [long-term emission fraction]	
AT	BIOL. [long-term biological removal fraction]	
AU	EMISS. [intermediate emission fraction]	
AV	BIOL. [intermediate biological removal fraction]	
AW	EFFLUENT [annual effluent fraction]	NON-AERATED
AX	EMISS. [annual emission fraction]	
AY	BIOL. [annual biological removal fraction]	
AZ	PHOTOL. & HYDROL. [annual fraction removed via photolysis and hydrolysis]	
BA	ADSORB. [annual fraction removed via adsorption]	
BB	AIR EMISSIONS (Mg/year)	
BC	EFFLUENT [annual effluent fraction]	AERATED
BD	EMISS. [annual emission fraction]	
BE	BIOL. [annual biological removal fraction]	
BF	PHOTOL. & HYDROL. [annual fraction removed via photolysis and hydrolysis]	
BG	ADSORB. [annual fraction removed via adsorption]	
BH	AIR EMISSIONS (Mg/year)	
BI	AQUEOUS [fraction remaining]	DISPOSAL IMPOUNDMENT
BJ	EMISS. [emission fraction for specified period]	
BK	BIOL. [biological removal fraction for specified period]	

EXHIBIT A-3. (continued)

Column	Column label [explanation]	
BL	PHOTOL. & HYDROL. [fraction removed via photolysis and hydrolysis for specified period]	↓
BM	ADSORB [fraction removed via adsorption for specified period]	
BN	Air emission (Mg/yr)	
BO	VO aqueous landfill	
BP	Biorate constant (g/s-g)	
BQ	K_o (g mol/cm^2-s) = [overall mass transfer coefficient (m/s)] x 5.56	
BR	SUM RATES DISPOSAL [sum of the various rate processes]	DISPOSAL IMPOUNDMENT
BS	lambda	
BT	CONC (g/cm^3)	
BU	BIO RATES (MO^{-1}) LANDFILL	LANDFILL

EXHIBIT A-3. (continued)

```
NON-AERATED WASTEWATER TREATMENT
WINDSPEED             4.47 m/s
depth                  1.8 m
AREA                  1500 m2
FLOW               0.00156 m3/s
VO inlet conc.          10 mg/l
TOTAL ORGANICS IN      250 mg/l
TOTAL BIORATE           19 mg/g bio-hr
ACTIVE BIOMASS           0 g/l
BIOMASS SOLIDS IN        0 m3/s
TEMPERATURE             25 deg. C

    TOTAL AIR EMISSIONS      0.39 Mg/yr

                         EFFLUENT EMISS. BIOL.  PHOTOL.ADSORB. air
 COMPOUND NAME                                  & HYDRO.      emiss.
______________________________________________________________(Mg/yr)
BENZENE                     0.199  0.801  0.000  0.000  0.000 0.3943
```

EXHIBIT A-4. NONAERATED MODEL INPUT PARAMETERS AND EMISSION RESULTS

```
NON-AERATED WASTEWATER TREATMENT
WINDSPEED                4.47 m/s
depth                     1.8 m
AREA                     1500 m2
FLOW                  0.00156 m3/s
VO inlet conc.             10 mg/l
TOTAL ORGANICS IN         250 mg/l
TOTAL BIORATE              19 mg/g bio-hr
ACTIVE BIOMASS           0.05 g/l
BIOMASS SOLIDS IN           0 m3/s
TEMPERATURE                25 deg. C

    TOTAL AIR EMISSIONS       0.29 Mg/yr

                       EFFLUENT EMISS. BIOL.  PHOTOL.ADSORB. air
 COMPOUND NAME                                & HYDRO.       emiss.
________________________________________________________________(Mg/yr)
BENZENE                   0.146  0.587  0.267  0.000  0.000 0.2891
```

EXHIBIT A-5. NONAERATED MODEL INPUT PARAMETERS AND EMISSION RESULTS

```
AERATED WASTEWATER TREATMENT

WINDSPEED                   4.47 m/s
DEPTH                        1.8 m
AREA                        1500 m2
FLOW                      0.0031 m3/s
ACTIVE BIOMASS               0.3 g/l
BIOMASS SOLIDS IN              0 m3/s
VO INLET CONC.                10 mg/l
TOTAL ORGANICS IN            250 mg/l
TOTAL BIORATE                 19 mg/g bio-hr
FRACT. AGITATED             0.24
SUBMERGED AIR FLOW             0 m3/s
Number' impellers              1
Oxygen trans. rat.             3 lbO2/h-hp
POWR (total)                  75 HP
Trans corr factor           0.83
Temperature                   25 deg C
impeller dia                  61 cm
impeller speed               126 rad/s

    TOTAL AIR EMISSIONS          0.97 Mg/yr

                                   RELATIVE AERATED WASTEWATER VOC PAT
                         EFFLUENT EMISS. BIOL.  PHOTOL.ADSORB. air
 COMPOUND NAME                                  & HYDRO.       emiss.
______________________________________________________________(Mg/yr)
BENZENE                     0.002  0.987  0.011  0.000  0.000  0.9655
```

EXHIBIT A-6. AERATED MODEL INPUT PARAMETERS AND EMISSION RESULTS FOR MECHANICALLY AERATED TREATMENT IMPOUNDMENT

```
AERATED WASTEWATER TREATMENT

WINDSPEED             4.47 m/s
DEPTH                    4 m
AREA                    27 m2
FLOW                0.0075 m3/s
ACTIVE BIOMASS           4 g/l
BIOMASS SOLIDS IN        0 m3/s
VO INLET CONC.          10 mg/l
TOTAL ORGANICS IN      250 mg/l
TOTAL BIORATE           19 mg/g bio-hr
FRACT. AGITATED       0.53
SUBMERGED AIR FLOW       0 m3/s
Number impellers         1
Oxygen trans. rat.       3 lbO2/h-hp
POWR (total)           7.5 HP
Trans corr factor     0.83
Temperature             25 deg C
impeller dia            61 cm
impeller speed         126 rad/s

    TOTAL AIR EMISSIONS       1.96 Mg/yr


                                  RELATIVE AERATED WASTEWATER VOC PAT
                         EFFLUENT EMISS. BIOL.  PHOTOL.ADSORB. air
 COMPOUND NAME                                  & HYDRO.      emiss.
______________________________________________________________(Mg/yr)
BENZENE                     0.078  0.827  0.095  0.000  0.000 1.9582
```

EXHIBIT A-7. AERATED MODEL INPUT PARAMETERS AND EMISSION RESULTS FOR ACTIVATED SLUDGE UNIT

```
AERATED WASTEWATER TREATMENT

WINDSPEED             4.47 m/s
DEPTH                    4 m
AREA                    27 m2
FLOW                0.0075 m3/s
ACTIVE BIOMASS           4 g/l
BIOMASS SOLIDS IN        0 m3/s
VO INLET CONC.          10 mg/l
TOTAL ORGANICS IN      250 mg/l
TOTAL BIORATE           19 mg/g bio-hr
FRACT. AGITATED          0
SUBMERGED AIR FLOW    0.04 m3/s
Number impellers         1
Oxygen trans. rat.       3 lbO2/h-hp
POWR (total)           7.5 HP
Trans corr factor     0.83
Temperature             25 deg C
impeller dia            61 cm
impeller speed         126 rad/s

    TOTAL AIR EMISSIONS      0.84 Mg/yr


                                  RELATIVE AERATED WASTEWATER VOC PAT
                         EFFLUENT EMISS. BIOL.  PHOTOL.ADSORB. air
 COMPOUND NAME                                  & HYDRO.      emiss.
______________________________________________________________(Mg/yr)
BENZENE                     0.291  0.355  0.354  0.000  0.000 0.8413
```

EXHIBIT A-8. AERATED MODEL INPUT PARAMETERS AND EMISSION RESULTS FOR DIFFUSED AIR-ACTIVATED SLUDGE UNIT

```
LAND TREATMENT MODEL DATA
(land treatment)
L,Loading (g oil/cc soil)          0.036
Enter Ci x 10^6   VO ppmw           2000
l,Depth (cm)                          20
Total porosity                      0.61
Air Porosity (default=0)             0.5
MW oil                               282
VO diss. in water, enter 1             0
Time of calc. (days)              365.25
Biodegradation, enter 1                1
Temperature (Deg. C)                  25
Wind Speed (m/s)                    4.47
Area (m2)                          25000

                        LANDTREATMENT      INTERMEDIATE TIME
                        FRACTION LOST           365.25  days
 COMPOUND NAME          AIR       BIOL.    AIR           BIOL.
__________________________________________ _____________________
BENZENE                     0.903     0.097        0.903     0.097
```

EXHIBIT A-9. LAND TREATMENT MODEL INPUT PARAMETERS AND EMISSION RESULTS FOR LAND TREATMENT SOIL

LAND TREATMENT MODEL DATA
(land treatment)

L,Loading (g oil/cc soil)	0.036
Enter Ci x 10^6 VO ppmw	2000
l,Depth (cm)	20
Total porosity	0.61
Air Porosity (default=0)	0.5
MW oil	282
VO diss. in water, enter 1	0
Time of calc. (days)	365.25
Biodegradation, enter 1	1
Temperature (Deg. C)	25
Wind Speed (m/s)	4.47
Area (m2)	25000

	LANDTREATMENT EMISSION RATES (g/cm2-s)				
	TIME (hours)				
COMPOUND NAME	0.25	1	4	12	48
BENZENE	2.89E-08	1.46E-08	7.28E-09	4.16E-09	1.98E-09

EXHIBIT A-10. LAND TREATMENT MODEL INPUT PARAMETERS AND SHORT-TERM EMISSION RESULTS FOR LAND TREATMENT SOIL

```
LAND TREATMENT MODEL DATA
(open landfill, waste pile)
L,Loading (g oil/cc soil)        0.464
Enter Ci x 10^6   VO ppmw       500000
l,Depth (cm)                       229
Total porosity                     0.5
Air Porosity (default=0)          0.25
MW oil                             147
VO diss. in water, enter 1           0
Time of calc. (days)            365.25
Biodegradation, enter 1              0
Temperature (Deg. C)                25
Wind Speed (m/s)                  4.47
Area (m2)                        14200

                              LANDTREATMENT      INTERMEDIATE TIME
                              FRACTION LOST           365.25  days
 COMPOUND NAME                AIR      BIOL.     AIR            BIOL.
____________________________________________    _______________________
CHLOROFORM                       1.000    0.000          0.053     0.000
```

EXHIBIT A-11. LAND TREATMENT MODEL INPUT PARAMETERS AND EMISSION RESULTS FOR OPEN LANDFILLS AND WASTEPILES

```
     DISPOSAL IMPOUNDMENT
       (no outlet flow)
WINDSPEED                 4.47 m/s
DEPTH                      1.8 m
AREA                      9000 m2
ACTIVE BIOMASS            0.05 g/l
BIOMASS SOLIDS IN            0 m3/s
VO INLET CONC.              10 mg/l
TOTAL ORGANICS IN          250 mg/l
TOTAL BIORATE               19 mg/g bio-hr
TIME FOR EMISSIONS           6 months
SUBMERGED AIR FLOW           0 m3/s
TEMPERATURE                 25 deg. C

    TOTAL AIR EMISSIONS  2.43E-01 Mg/yr

                          DISPOSAL IMPOUND. VO EMISSIONS     6 MONTHS
                          AQUEOUS  EMISS. BIOL.  PHOTOL.ADSORB. air
 COMPOUND NAME                                   & HYDRO.       emiss.
_____________________________________________________________(Mg/yr)
BENZENE                      0.000  0.751  0.249  0.000  0.000 0.243171
```

EXHIBIT A-12. DISPOSAL IMPOUNDMENT INPUT PARAMETERS AND EMISSION RESULTS

```
CLOSED LANDFILL

A, LF area  (cm2)           1.4170E+08
l, cap thickness (cm)              107
ea, cap air porosity              0.08
et,cap total porosity             0.41
T, avg. LF temp. (C)                15
efw, waste porosity               0.25
Pref, ref. pressure (mbar)        1013
P1, new pressure (mbar)           1009
Tref, reference temp. (C)           15
T1, new temp. (C)                   15
dt,bar.pump time int.(s)         86400
weight fraction oil                0.2
weight fraction water              0.6
weight fraction VO                 0.2
W, liquid in waste (g/cm3)        1.16
mwt oil                            147
t, time of calc. (mo.)              12
D, depth of waste (cm)             457
CC/GVOC CONV                      1750
active biomass (g/cc)         0.00E+00
VO diss. in water, enter 1           0
rho-liquid,density (g/cm3)           1
MW-liquid, (g/g mol)                18

                           CLOSED LANDFILL AIR EMISSIONS
                                           EMISSION RATES
 COMPOUND NAME           EMISS.   BIOL.           12 months
_________________________FRACTION FRACTION AVERAGE  INST.
CHLOROFORM                  1.000    0.000 12.99431 12.98869
```

EXHIBIT A-13. CLOSED LANDFILL MODEL INPUT PARAMETERS AND EMISSION RESULTS

```
OIL FILM SURFACE

WINDSPEED   (m/s)                        4.47
depth         (m)                       0.072
AREA         (m2)                       25000
FLOW       (m3/s)                           0
VO conc. in oil    (mg/l)                 200
oil (fraction of waste)                     1
molecular weight of oil                   282
density of oil (g/cc)                       1
Enter months for disposal               0.033
Temperature (deg C)                        25


                                 OIL FILM
 COMPOUND NAME                   emissions
________________________________fraction
BUTANOL-1                        0.494451
```

EXHIBIT A-14. OIL FILM SURFACE MODEL INPUT PARAMETERS AND EMISSION RESULTS

Selection	Options (explanation)
DATA-FORMS	(Go to data-entry forms)
	IMPOUND (Go to the data entry form MENU for impoundments)
	NON-AERATED (Go to the data entry form for flowthrough impoundments)
	DIFFUSED (Go to the data entry form for diffused-air disposal)
	FILM (Go to the data entry form for oil films)
	DISPOSAL IMPOUNDMENTS (Go to the data entry form for disposal impoundments)
	QUIT
	AERATED (Go to the data entry form for activated sludge processes)
	CLOSED-LANDFILL (Go to the data entry form for capped landfill)
	OPEN-LF/WP (Go to the data entry form for open landfill/wastepile)
	LAND-TREAT (Go to the data entry form for land application of wastes)
	DEFAULT (Replace parameters with default parameters)
	Municipal (municipal waste aerated impoundment parameters)
	Aerated (default aerated model parameters)
	Non-aerated (default non-aerated model parameters)
	Landfill (default landfill model parameters)
	Land-tr. (default land treatment model parameters)
	Open lf (set open landfill/wastepile to default)

EXHIBIT A-15. ALTERNATIVE COMMAND MENU

- Disposal (default disposal impoundment model parameters)
- Quit (Return to data forms menu)

QUIT (Return to main menu)

VIEW (Go to a portion of the worksheet)

IMPOUND. (Go to the MENU for impoundments)

- NON-AERATED (Go to the calculations for flowthrough impoundments)
- DIFFUSED (Go to the calculations for diffused air disposal)
- FILM (Go to the calculations for oil films)
- DISPOSAL (Go to the calculations for disposal impoundments)
- QUIT

AERATED (View results)

OPEN LF/WP (Use land treatment model to simulate an open landfill)

CLOSED-LF (View calculations for a closed landfill)

LAND-TREAT (View results)

TOTAL-EMISSIONS (View the results for long-term integrated emissions)

EMISSION-RATE (View the results for initial emission rates)

RETURN (Main menu)

GRAPH (VIEW GRAPH)

- LANDFILL (View a graph)
- LAND-TREAT (View a graph)

EXHIBIT A-15. (continued)

- NON-AERATED (View a graph)
- AERATED (View a graph)
- DISPOSAL (View a graph)
- QUIT

SORT (Rearrange the order of the compound listings)

- SELECT (Sort by selected compounds)
- ALPHABETIC (Sort alphabetically)
- BIOLOGICAL (Sort in descending biological rates)
- CLASS (Sort by compound type)
- V-PRESSURE (SORT BY VAPOR PRESSURE)
- QUIT (RETURN TO MENU)

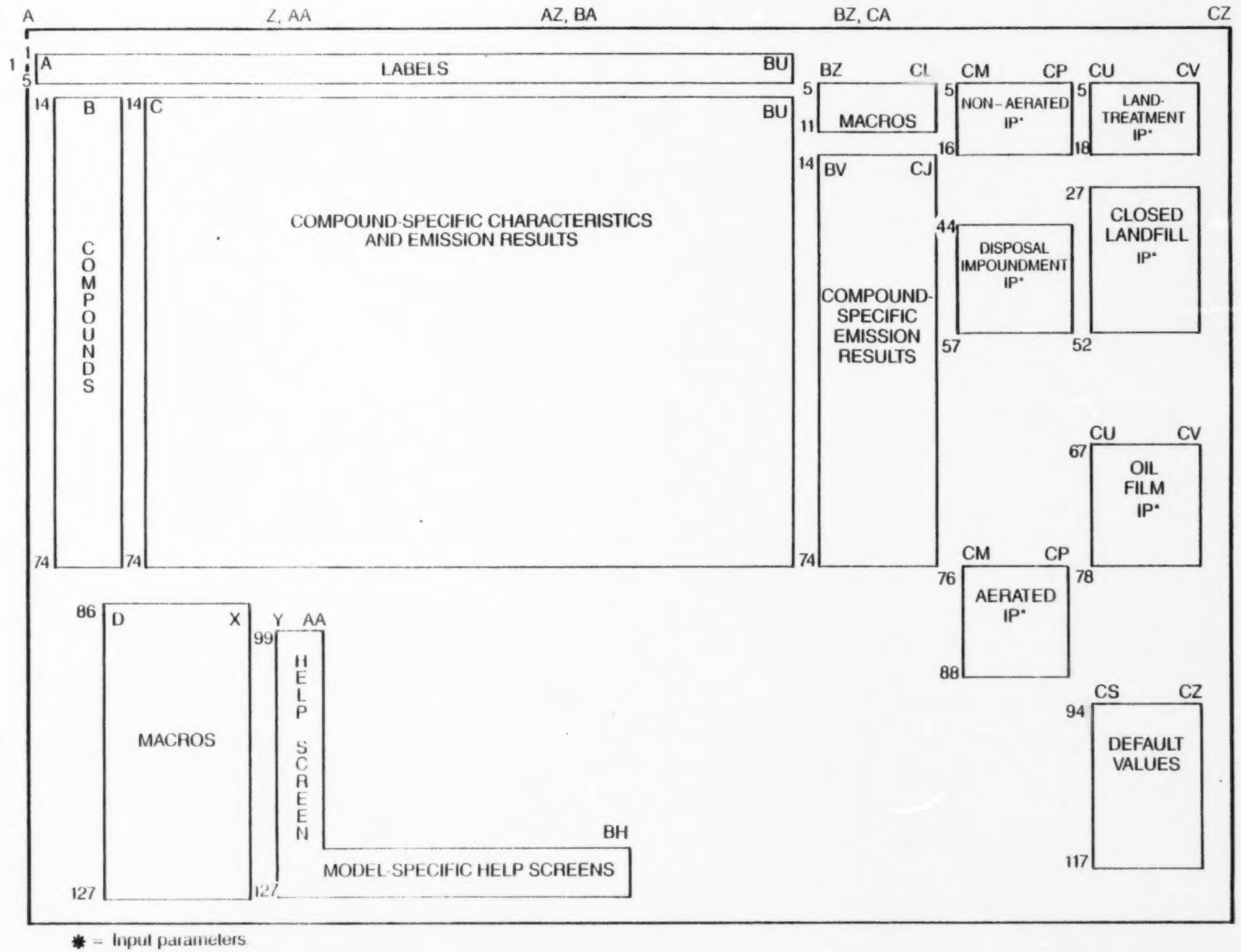
PRINT (Print a portion of the worksheet)

- LAND-TREAT (Print land treatment, open landfill, or wastepile results)
- LONG-TERM (Print long-term environmental fate)
- SHORT-TERM (Print short-term emission estimates)
- DISPOSAL (Print disposal lagoon results)
- AERATED (Print aerated process results)
- LANDFILL (Print closed landfill results)
- NON-AER. (Print non-aerated impoundment results)
- DATA (Print data summaries)
  - BIORATE (Print biorate data)
  - LAND-TREAT (Print land treatment data)
  - DATA (Print chemdat information)

EXHIBIT A-15. (continued)

	GRAPH (Put a graph file on the disk for later printing)
	FILM (Print thin film lagoon results)
SELECT	(Select which models are to be used)
HELP	(Look at an instructional screen)
	GENERAL (View general information)
	MENU (Return to the main menu)
	HELP (Select another help screen)
	LANDTREAT (Information for the use of the land treatment models)
	MENU (Return to the main menu)
	HELP (Select another help screen)
	LANDFILL (Information for the use of the landfill model)
	MENU (Return to the main menu)
	HELP (Select another help screen)
	BIO-RATE (Information for the use of the biological reaction rates)
	MENU (Return to the main menu)
	HELP (Select another help screen)
	IMPOUND (Information for the use of the impoundment models)
	MENU (Return to the main menu)
	HELP (Select another help screen)
	MENU (Return to the main menu)
QUIT	(Return to spreadsheet command mode)

EXHIBIT A-15. (continued)


A
Z, AA
AZ, BA
BZ, CA
CZ
1
5
A
LABELS
BU
14
B
COMPOUNDS
74
14
C
BU
COMPOUND-SPECIFIC CHARACTERISTICS AND EMISSION RESULTS
74
BZ
CL
5
MACROS
11
14
BV
CJ
COMPOUND-SPECIFIC EMISSION RESULTS
74
CM
CP
5
NON-AERATED IP*
16
CU
CV
5
LAND-TREATMENT IP*
18
27
CLOSED LANDFILL IP*
52
44
DISPOSAL IMPOUNDMENT IP*
57
CU
CV
67
OIL FILM IP*
78
CM
CP
76
AERATED IP*
88
CS
CZ
94
DEFAULT VALUES
117
86
D
X
MACROS
127
Y
AA
99
HELP SCREEN
BH
MODEL-SPECIFIC HELP SCREENS
127
* = Input parameters

ATTACHMENT A. GENERALIZED LAYOUT OF CHEMDAT6 SPREADSHEET

APPENDIX B

A GUIDE THROUGH THE LITERATURE

APPENDIX B

A GUIDE THROUGH THE LITERATURE

B.1 INTRODUCTION

There is concern that volatilization of organic compounds (VO) from hazardous waste treatment, storage, and disposal facilities (TSDF) poses a public health problem. These VO emissions may adversely affect ambient air quality in or around a hazardous waste TSDF. However, there are other competing mechanisms or pathways through which VO can leave hazardous waste facilities. These include adsorption, migration, runoff, biological or chemical degradation, hydrolysis, oxidation, and hydroxyl radical reaction. Consequently, the potential hazard of volatilization should be assessed in relation to the potential importance of these other pathways.

Hazardous waste TSDF include, among others, surface impoundments, landfarms, landfills, and wastewater treatment plants. The important competing pathways for each hazardous waste site have been identified in earlier sections of this report. This evaluation has been based on field and laboratory measurements as well as predictive or mathematical models of these pathways. This appendix supplements the body of the report; it serves to direct the reader through the literature concerning VO pathways from hazardous waste TSDF.

For the convenience of the reader, a comprehensive source list is presented in Appendix C of this report. In addition to the references cited in this appendix and in the individual sections of the report, this bibliography lists other literature of interest for VO pathways and TSDF emission models.

B.2 SURFACE IMPOUNDMENTS

B.2.1 Volatilization

Direct measurement of volatilization rates from surface impoundments is extremely complicated. Hwang and Thibodeaux[1] reviewed the concentration profile and plume mapping technique and proposed a new method requiring fewer concentration measurements. This latter technique has yet to gain popularity. Thibodeaux et al.[2] used the concentration profile technique to measure the rate at which selected VO were emitted to the air from basins in the pulp and paper industry. The ranges of the average flux for methanol and acetone were 1.4 to 3.8 $ng/cm^2 \cdot s$ and 0.028 to 0.10 $ng/cm^2 \cdot s$, respectively, which were higher than background. Radian[3] obtained emission rates from four different hazardous waste sites containing surface impoundments as well as landfills and landfarms. They used the concentration profile, transect, materials balance, and vent sampling approaches. These methods[4,5] are also applicable to other nonpoint source hazardous waste facilities such as landfills and landfarms.

Volatilization rates from surface impoundments can be estimated via mathematical models. Mackay and Leinonen[6] predicted air emissions from nonaerated surface impoundments receiving influent irregularly (unsteady state). The liquid and gas mass transfer coefficients in this model were modified by Mackay and Yeun.[7] Thibodeaux et al.[8] developed predictive models for both aerated and nonaerated steady-state surface impoundments. DeWolf and Wetherold[9] critiqued these models and presented a protocol for their proper use. Shen[10] modified the nonaerated model of Thibodeaux et al.[11] In an extensive review of these and other predictive models, GCA[12] judged the theoretical work of Thibodeaux et al.[13] and Mackay and Leinonen[14] as most suitable for predicting air emissions from surface impoundments.

The use of these mathematical models for predicting volatile emissions is less expensive and faster than actual field measurements. However, to be cost-effective, these mathematical models must provide accurate estimates of volatilization rates. It is disappointing to note that relatively few validation studies are reported in the literature. A description of these follows.

Hwang[15] compared predicted and measured emission rates of toluene and 1,1,1-trichloroethane from an evaporation pond. The transect method was used for field measurements, and the models summarized in Hwang[16] provided the predicted rates. For each organic compound, the predicted result was within the confidence limits of the average measured result. Balfour et al.[17] used the Thibodeaux et al.[18] model to predict emissions from these surface impoundments. Emission rates were measured via the flux chamber in all three ponds as well as via the concentration profile in the third pond. In this latter pond, the emission rate of most compounds as determined using the flux chamber was statistically greater than that determined using the concentration profile. Furthermore, results of a comparison of measured versus predicted emission rates were inconclusive. Vaught[19] used the Springer et al.[20] and Mackay and Yeun[21] approaches to predict air emissions from quiescent surface impoundments. He concluded that volatilization rates predicted from the Mackay and Yeun model were comparable to rates measured via the flux chamber. In contrast, the predicted rates from Springer et al. exceeded the measured rates.

B.2.2 Other Pathways

The role of other pathways in the removal of VO from surface impoundments has not been addressed extensively in the literature. However, biological removal mechanisms associated with stabilization ponds and lagoons[22] will be applicable where conditions of pH, temperature, and nutrient levels are suitable for biological growth.

B.3 LAND TREATMENT

For the past 25 years, the petroleum industry has operated land treatment, sludge farming, and land disposal facilities. The pharmaceutical and organic chemical manufacturers recently have considered this method of hazardous waste disposal because of its comparatively reasonable cost, simplicity, and use of natural processes. How does a land treatment effectively and safely treat and dispose of VO? The purpose of land treatment is to exploit the microbiological actions of the upper soil layer to degrade toxic organic material at a controlled rate. Although photodegradation takes place in a land treatment facility,[23] the short time that the materials are exposed to direct sunlight and the screening effect of the oil in which hazardous materials are suspended make this pathway negligible. Several other pathways may exist: volatilization, runoff, and leaching.[24,25] However, these latter mechanisms do not occur at a properly sited, operated, and maintained RCRA-permitted land treatment facility.

B.3.1 Degradation

The chemical structure of the hazardous waste, application and mixing techniques, and soil characteristics (texture, temperature, moisture content, oxygen level, nutrient level, pH, and the kind and number of microbes) affect biodegradation.[26,27] Although biodegradation is purported to be the principal mechanism for removal of organic compounds by land treatment, only a few experiments have attempted to quantify the resulting removal. A laboratory simulation of land treatment of oily sludge revealed that 85 percent of the polynuclear aromatics degraded.[28] Results from Snyder et al.[29] are comparable: oil removal on fertilized plots approached 80 percent at 1 year postapplication.

Mathematical models for degradation could not be found in the literature.

B.3.2 Volatilization

Techniques for direct measurement of volatilization at landfarms[30,31] were discussed previously. Exogenous factors affecting volatilization in land treatment include properties of the soil, waste application techniques, mixing schedules, and atmospheric conditions.[32,33,34]

Farmer and Letey[35] proposed five gradient models for pesticide volatilization rates from the soil based on diffusion laws. The models accommodate soil-incorporated pesticides with and without significant mobility in flowing water. With nonincorporated pesticides, vapor density relationships and air flow rate rather than movement in the soil control the volatilization rate. These approaches do not, however, accommodate subsurface injection. Thibodeaux and Hwang[36] developed a gradientless model of air emissions from petroluem waste landfarms. Their approach accurately predicted the volatilization of dieldrin reported in Farmer and Letey[37] and is considered most suitable for estimating air emissions from land treatment.

B.3.3 Migration and Runoff

Migration and runoff of VO from a landfarm may occur after improper application or treatment of the hazardous waste. A description of factors affecting these two pathways appeared in Reference 38. Results from a laboratory study of refinery and petrochemical sludge[39] suggested that the presence of hazardous waste in runoff decreases with time after application. In addition, leachate water collected 1.5 meters below the subsurface was essentially free of toxic components.

However, as previously mentioned, migration and runoff do not occur at a properly sited, operated, and maintained RCRA-permitted land treatment facility. This paragraph is included for the sake of completeness.

B.4 LANDFILLS

B.4.1 Volatilization

Direct measurements of VO emissions from landfills are possible. During field tests conducted for EPA's Office of Air Quality Planning and Standards (OAQPS), Radian[40] measured air emissions from landfills at three of the four monitored hazardous waste TSDF. Markle et al.[41] collected air samples from three landfills representative of those used by the polyvinyl chloride industry for health hazard evaluations. To compare the efficiencies of water and soil coverings in reducing volatilization, Farmer et al.[42] measured emission rates from simulated landfills.

Numerous equations also have been developed to model VO emissions from hazardous waste landfills. The procedure of Farmer et al.[43] based on Fick's law for steady-state diffusion, estimates emission from covered or buried landfills. This was later modified by Shen.[44] Thibodeaux's[45] emission models differentiate covered landfills by the presence or absence of internal gas generation. Another approach[46] incorporates time-varying atmospheric pressure into the emission model. Volatilization rates from landfills with no covering, i.e., open dumps, were modeled by Shen.[47] DeWolf and Wetherold[48] recommend Shen's[49] emission model for covered landfills. GCA, in their excellent comprehensive review of these and other emission models, prefers the work of Farmer et al.[50] and Thibodeaux.[51]

Field validation of these mathematical models has not been reported in the literature. Despite this, Baker and Mackay[52] employed Shen's[53] model in their protocol to evaluate toxic air pollution downwind of hazardous waste landfills.

B.4.2 Migration

Several scientists have investigated the potential problem of migration of toxic contaminants from landfills. Rovers and Farquhar[54] suggested that the production of leachate within a landfill is not uncommon. However, the migration of harmful compounds through adjacent soils is not significant. Shen and Tofflemire[55] reported that annual losses of PCB to migration from uncovered landfills in the Hudson River Basin (New York) were substantially less than losses to volatilization.

B.4.3 Other Pathways

The impact of other pathways is not discussed quantitatively in the literature.

B.5 WASTEWATER TREATMENT PLANT EFFLUENT

A description of the pathways operating in a wastewater treatment plant is complicated by the number of different treatment systems. There are closed tanks and open tanks (with and without mixing). Air emissions from closed tanks occur during venting.

E. C. Jordan[56] and Burns and Roe[57,58] examined the fate of priority toxic pollutants in publicly owned treatment plants. They observed a decrease in VO concentrations across the activated sludge process and a lack of pollutant accumulation in the waste-activated sludge. This suggests that VO are substantially air-stripped or biodegraded during secondary treatment. Results from the controlled laboratory experiments of Roberts et al.[59] imply that organic solutes more likely volatilize during wastewater treatment with surface aeration than with bubble aeration. Lurker et al.[60] examined how aeration rate, suspended particle concentration, and detergent concentration influence aerial organic chemical release from an activated sewage treatment process.

The nonaerated open tank system is similar to the nonaerated surface impoundment discussed previously; see Section B.2.1 for a discussion of the corresponding emission rate models. Similarly, open tank wastewater treatment processes with mixing can be estimated from Thibodeaux et al.[61] Hwang[62] went a step further in his activated sludge surface aeration model. His approach was to estimate pollutant removal by degradation, adsorption, and air stripping via a mass balance equation. Like Hwang and Thibodeaux et al., Freeman[63] considered air stripping losses at the air-water interface. Unlike Hwang, however, he viewed the adsorption pathway as insignificant and, thus, ignored it. In an entirely different approach, Freeman[64,65] modeled the mass transfer of a toxic compound into the bubbles of the aerated system (diffused air [subsurface] activated sludge model). The structure of these and other models was critiqued in GCA.[66]

Allen et al.[67] presented models of VO losses at each process encountered in wastewater treatment systems. The models include a methodology for estimating the relative importance of competing pathways. Additionally, these investigators compared the loss of volatiles obtained from field tests at several treatment facilities[68] and from these mathematical models. The models predict VO losses due to biodegradation or volatilization in close agreement with the field data. Results from other validation studies are not as consistent. Predicted emission rates from aerated surface impoundments at two wastewater treatment plants were generally larger than measured values.[69] The difference between measured and predicted emission rates in Cox et al.[70] appears to be a function of the type of compound and the presence of aerators.

B.6 SUMMARY

This appendix serves to guide the reader through the literature concerning VO pathways from hazardous waste TSDF. The pathways of interest include volatilization, adsorption, migration, runoff, biological or chemical degradation, hydrolysis, oxidation, and hydroxyl radical reaction. The hazardous waste TSDF considered are surface impoundments, landfills, landfarms, and wastewater treatment plants. The body of this report expands on the pathways and models most applicable to current research.

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APPENDIX C

COMPREHENSIVE SOURCE LIST

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APPENDIX D

PROPERTIES FOR COMPOUNDS OF INTEREST

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PROPERTIES FOR COMPOUNDS OF INTEREST

This appendix contains compound-specific properties of about 700 chemicals not included in CHEMDAT6. These data, presented as a source of information, can be easily incorporated into CHEMDAT6. Consequently, this appendix greatly increases the utility of CHEMDAT6. The chemical "universe" tested in this appendix represents those chemicals that could be encountered in TSDF and that are useful for calculating emission rates for the facilities modeled in the body of this report. The list was extracted from the GCA Physical/Chemical Database, WET model stream compositions, and the Industrial Studies Database.

The compounds listed in this appendix were not originally included in CHEMDAT6 because their inclusion would seriously slow the execution time of the program, the memory requirements would prevent the program from being run on many machines, and because the data are not complete for some of the chemicals. Compounds included in the CHEMDAT6 program were selected on the basis of the estimated frequency with which they are found in hazardous wastes and on their position in prioritized lists of pollutants.

The following properties are given for each chemical (listed by name and Chemical Abstract Source [CAS] number):

- Molecular weight
- Density
- Vapor pressure at 25 °C
- Solubility
- Henry's law constant
- Diffusion coefficient in water

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- Diffusion coefficient in air
- Boiling point
- Coefficients for the Antoine equation for estimating vapor pressure at temperatures other than 25 °C
- Cancer unit risk value
- Allowable daily intake in air
- Ratio of biochemical oxygen demand to chemical oxygen demand.

To estimate vapor pressures at temperatures other than 25 °C, the Antoine equation coefficients are used with the following equation:

$$\log_{(10)} \text{Vapor Pressure (mm Hg)} = A - \frac{B}{T + C}$$

where

A, B, and C = the Antoine equation coefficient

T = temperature in °C.

Two approaches may be used to introduce a new compound and its properties into CHEMDAT6. First, the data for one compound in CHEMDAT6 may be replaced with data for the compound of interest in the columns specified above. With this approach, the list of compounds in CHEMDAT6 remains constant at 62. The second approach involves appending the new compound and its properties to the existing list of chemicals in CHEMDAT6. All the equations/calculations must then be copied from one of the existing rows via Lotus 1,2,3 into the appropriate cells in the new row of the spreadsheet. As mentioned above, the inclusion in CHEMDAT6 of all or a large part of the chemicals listed in this appendix could result in increasing the time required to exercise CHEMDAT6 and could prevent its use on some microcomputers.

The properties of interest listed above, with the exception of the CAS number, mimic those in columns B, D-M, and Q of the CHEMDAT6 spreadsheet.

COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
1,1-CHLOROPHENYLETHANOL	3391-10-4	156.53			2	7.83E-03									
1,1-DIETHYLUREA	634-95-7	116.07			2000	5.80E-06									
1,1-DIPHENYLETHANE		182.00			20	9.10E-04									
1,1-DIPHENYLETHANOL	599-67-7	198.14			10000	1.98E-06									
1,2-BENZANTHRACENE	56-55-3	228.30	1.11	1.5E-07		1.38E-09	9.00E-06	5.10E-02	58.9				6.9E-06		
1,2-DIBROMO-3 CHLOROPROPANE	96-12-8	236.30			1000	2.36E-05									
1,2-DICHLORO-2-BUTENE		124.90			0.02	1.56E+03									
1,3-CYCLOPENTADIENE	542-92-7	66.10			2	3.31E-03									
1,3-DIPHENYLBUTADIENE	886-65-7	206.16			10	2.06E-03									
1-ACETYL-2 THIOUREA	591-08-2	118.17		0.004											
1-BROMO-4-CHLOROCYCLOHEXANE		199.50			0.2	9.98E-02									
1-CHLORO-2,2-DIBROMOETHANE		222.5		1520	2	2.23E+02									
1-CHLORO-2-NITROBENZENE	88-73-3	157.56			2	7.88E-03									
1-METHYL-2 METHOXYAZIRIDINE		87.00			20000	4.35E-07									
1-METHYL-3-ACETYLCYCLOPENTADIENE		106.00			2	5.30E-03									
2,2,4-TRIMETHYLPENTANE	540-84-1	114.22		40.6	0.56	1.09E+01									
2,3,5-TRIMETHYL-4-NITROANILINE		180.00			2	9.00E-03									
2,3,7,8-TETRACHLORODIBENZOFURAN		306.00			2	1.53E-04									
2,4,5-TRICHLOROPHENOXY-ACETIC ACID	93-76-5	255.49		0.076	10	2.55E-03									
2,4,6-TRICHLORO-1,3,5-TRIAZINE	108-77-0	184.41			0.2	9.22E-04									
2,4-DIAMINO-5-SULFONYL BENZYL		185		0.076	25000	7.40E-07									
2,4-DIMETHYL-1-NITROBENZENE	25168-04-1	151.18			2	7.56E-03									
2,6 DICHLOROSTYRENE	28469-92-3	172.00			2	8.60E-03									
2,6-DINITROTOLUENE	606-20-2	182.14			20	9.11E-06									
2-ACETYLFURAN	1192-62-7	110.06			100	1.10E-04									
2-AMINO-3-CHLORO-5-PHENYLCYCLOHEXANONE		163.5		0.076		4.13E-06									
2-AMINO-4-CHLORO-6-CYANOPYRIDINE		155.00			50	3.10E-04									
2-AMINO 4 CHLOROPYRIDINE	1072-98-6	128.56		190	10000	3.21E-03									
2-AMINO-4-NITROBENZYL ALCOHOL		152.00			2500	6.08E-06									
2-AMINO-4-NITROTOLUENE	99-55-8	152.17			2	7.61E-03									
2-AMINO-5-CHLOROPYRIDINE	1072-98-6	128.56			10000										
2-BROMO-3-CHLOROBUTADIENE		169.00			2	8.45E-03									
2-BROMO-4-CHLORO-6-CYANOBENZYL ALCOHOL		189.00			1000	1.89E-05									
2-BROMO-4-CYANOMETHYL BENZOATE		240.00			0.2	1.20E-01									
2-CHLORO-3-NITRO-5-PHENYLCYCLOHEXANE		188.5		0.076		4.13E-06									
2-CHLORO-4-AMINOCOUMARAN-6-CARBOXYLIC ACID		213.5		0.076	2000	1.07E-05									
2-CHLORO-4-CYANOBENZYL ALCOHOL		153.00			2500	6.12E-06									
2-CHLORO-4-METHOXY-6-AMINOBENZOIC ACID		200.00			50	4.00E-04									
2-CHLORO-4-NITROANISOLE		187.5		0.076	2	9.38E-03									
2-CHLORO 4 PHENYLPYRIDINE		190.00			2000	9.50E-06									
2-CHLORO-5-AMINO-3-PYRIDINE CARBOXYLIC ACID AMIDE		183.00			50	3.66E-04									
2-CHLOROALLYL ALCOHOL	5976-47-6	92.53		1.5	10000	1.83E-05			146.0						
2-CHLOROBUTADIENE-1,3	126-99-8	88.50	0.96	288	100	3.35E-01			59.4	6.161	783.45	179.7			
2-CHLOROCOUMARAN	2051-59-4	180.59			2	9.03E-03									
2-CHLOROCYCLOHEXANOL	1561-86-0	134.61			50	2.69E-04									
2-CHLOROETHANOL	107-07-3	80.52		10	100000	1.96E-05									
2-CHLOROPYRIDINE	109-09-1	113.55		1	100	1.49E-03									
2 CYCLOHEXYL-2,2 DIPHENYLETHYLAMINE		257.00			100	2.57E-04									
2-HYDROXY-6 METHYLPYRIDINE-3 CARBOXYLIC	38116-61-9	153.14			50	3.06E-04									
2-IODOCOUMARAN		246		0.076	2	1.23E-02									
2-METHYL-1 PENTENE	763-29-1	84.90			2	1.05E+01									

COMPOUND NAME	CAS #	M.W.	*DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
2-METHYL-4-NITROBENZYL ALCOHOL	23876-13-3	167.16			5000	3.34E-06									
2-METHYLACETONITRILE	75-86-5	85.12		0.8	200	3.59E-01									
2-METHYLCOUMARAN	607-71-6	160.18			2	8.01E-03									
2-METHYLFURAN	534-22-5	82.11			3000	2.74E-06									
2-METHYLPROPENE	115-11-7	56.00			2	7.00E+00									
2-METHYLTETRAHYDROFURAN		87.00			1000	2.18E-02									
2-NITROPROPANE	79-46-9	89.09			100000	2.23E-04									
2-PROPYN-1-OL	107-19-7	56.06		11.6	100000	8.56E-06									
2-THIOPROPIONAMIDE		103.00			2000	5.15E-06									
3,4-BENZOPYRENE	50-32-8	252.32	1.11	5.68E-04		1.38E-09	9.00E-06	4.30E-02	312.0						
3,4-DICHLOROTETRAHYDROFURAN	3511-19-1	141.00			100000	1.41E-07									
3-ACETYL-5-HYDROXYPIPERIDINE		140.00			20000	7.00E-07									
3-ACETYLPIPERIDINE	618-42-8	125.00			100000	1.25E-07									
3-ACETYLPYRIDINE	1122-54-9	121.15			100	3.03E-01									
3-AMINOPROPIONITRILE	151-18-8	70.11		2	20000	9.23E-06									
3-BROMO-4-CYANOMETHYL BENZOATE		241.00			1	2.41E-02									
3-BROMOPROPIONITRILE	2417-90-5	133.98	1.615	0.076	10000	1.34E-06									
3-CHLORO-2,5-DIKETOPYRROLIDINE		133.50			200000	6.68E-08									
3-CHLORO-4-HYDROXYBIPHENYL	92-04-6	204.66		4	2	5.39E-01									
3-CHLORO-4-METHOXY-5-METHYL-N,N-DIMETHYLBENZAMIDE		211.00			10000	2.11E-06									
3-CHLORO-4-METHYL-N-METHYLBENZAMIDE		183.00			2000	9.15E-06									
3-CHLORO-5-CYANOTOLUENE		151.00			10	1.51E-03									
3-CHLORO-5-FLUOROTOLUENE	443-83-4	144.52			50	2.89E-04									
3-CHLORODIMETHYL PHTHALATE		229.00			0.2	1.15E-01									
3-CHLOROPROPIONITRILE	542-76-7	89.53		6	45000	1.57E-05									
3-CHLOROTETRAHYDROFURAN		121.00			100000	3.03E-04									
3-CYANOPYRIDINE	100-54-9	104.11			100	2.60E-01									
3-HYDROXY-4-METHYLTETRAHYDROFURAN		103.00			100000	2.58E-04									
3-HYDROXYPENTANE	584-02-1	88.70			55000	4.03E-04									
3-METHYLCHOLANTHRENE	56-49-5	268.36			2	1.34E-04									
3-NITRO-4-METHYLBENZOATE		195		0.076	20	9.75E-04									
4-ACETYLMETHYLPHTHALATE		236		0.00076	2	1.18E-04									
4-AMINO-2-CHLOROTOLUENE		140.00			2	7.00E-03									
4-AMINO-4'-CHLOROBIPHENYL		203.5		0.076	2	1.02E-02									
4-BROMOTOLUENE	106-38-7	171.00	1.3959	0.076	10	1.71E-03									
4-CHLORO-2-METHOXYBENZOIC ACID	57479-70-6	187.00			5	3.74E-03									
4-CHLORO-2-NITROBENZYL ALCOHOL	22996-18-5	187.00			5000	3.74E-06									
4-CHLORO-3-NITROANILINE	635-22-3	172.58			100	1.73E-04									
4-CHLORO-5-CYANOPHTHALIC ACID		225.5		0.076	1000	2.26E-05									
4-CHLORO-5-PHENOXYDIMETHYL PHTHALATE		320.00			0.2	1.60E-01									
4-CHLOROAZOBENZENE															
4-CHLOROCYCLOHEXANOL		134.6			10	1.35E-03									
4-CHLOROHYDROXYPHENYL METHYL BENZOIC ACID		262.5		0.076	2000	1.31E-05									
4-CHLOROPHTHALIC ANHYDRIDE		183.60			5000	3.67E-06									
4-CYANOMETHYL BENZOATE					2	1.20E-08									
4-CYANOMETHYLPHTHALATE		308		0.00076	2	1.54E-04									
4-CYANOTOLUENE	104-85-8	117.40			2	1.47E+01									
4-CYCLOHEXYLCYCLOHEXANONE	56025-96-8	80.32			2	4.02E-03									
4-HYDROXY-5-METHY DIMETHYL PHTHALATE		225.00			0.2	1.13E-01									
4-HYDROXYCYCLOHEXANONE		114		0.076		4.13E-06									
4-HYDROXYDIMETHYL PHTHALATE		210.00			0.2	1.05E-01									

COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
4-METHYL BENZYL ALCOHOL		139.00			1000	1.39E-05									
4-METHYL-3-NITROBENZYL ALCOHOL	40870-59-5	168.00			2500	6.72E-06									
4-METHYL-5-THIOACETYL-DIHYDRO-1,3-THIAZOLE		158		0.076	50	3.16E-04									
4-METHYL-TRIHYDRO-1,3-THIAZOLE		105.00			100	1.05E-04									
4-METHYLTHIOPHENOL	106-45-6	124.00		0.076		4.40E-07									
4-NITROSOBENZYL ALCOHOL		135.00			1000	1.35E-05									
4-PHENYLCYCLOHEXANONE	4894-75-1	175.00			2	8.75E-03									
4-SULFOPHTHALIC ANHYDRIDE		228	1.62	0.00076	10000	2.28E-08									
4-VINYLCYCLOHEXENE	100-40-3	108.20		25.8	2	1.84E+00									
5,5-DICHLORO-1,3-CYCLOPENTADIENE		134.50			0.2	6.73E-02									
5-AMINOMETHYL-3-ISOXAZOLOL	2763-96-4	114.1		0.1	200	7.51E-05									
5-CHLORO-1,3-CYCLOPENTADIENE		100.00			0.2	5.00E-02									
5-HYDROXY-1,3-CYCLOPENTADIENE		81.00			2	4.05E-03									
5-METHYL-1,3-CYCLOPENTADIENE	26519-91-5	80.14			0.2	4.01E-02									
5-METHYLFURFURAL	620-02-0	110.11			50000	2.20E-07									
ACENAPHTHENE	83-32-9	154.21	1.07	0.005	2	7.71E-03			278.0	7.728	2534.234	245.576			
ACENAPHTHYLENE	208-96-8	152.21			2	1.14E-04									
ACETALDEHYDE	75-07-0	44.05	0.79	760		9.50E-05	1.41E-05	1.24E-01	20.8	8.005	1600.017	291.809			
ACETAMIDE	60-35-5	59.07		1	650000	1.20E-07									
ACETIC ACID	64-19-7	60.05	1.05	15.41		6.27E-02	1.20E-05	1.13E-01	118.0	7.387	1533.313	222.309			0.310
ACETIC ANHYDRIDE	108-24-7	102.09	1.04	5.288		5.91E-06	9.33E-06	2.35E-01	139.6	7.149	1444.718	199.817			0.320
ACETONE	67-64-1	58.08	0.79	266		2.50E-05	1.14E-05	1.24E-01	56.2	7.117	1210.595	229.664		10000	0.550
ACETONITRILE	75-05-8	41.03	0.78	90		5.80E-06	1.66E-05	1.28E-01	81.6	7.119	1314.400	230.000			0.079
ACETOPHENONE	98-86-2	120.16	1.03	1		1.41E-05			202.3	9.135	2878.800	273.000			
ACETYL CHLORIDE	79-36-5	78.50	1.11	287.8			1.15E-05	9.90E-02	52.0	6.948	1115.954	223.554			
ACETYL DIETHYLMALONATE		194.00			1000	1.94E-05									
ACETYLENE	74-86-2	26.04		40	1085	1.26E-03									
ACROLEIN	107-02-8	56.06	0.84	244.2		5.66E-05	1.22E-05	1.05E-01	53.0					55	
ACRYLAMIDE	79-06-1	71.09	1.12	0.012		5.20E-10	1.06E-05	9.70E-02	87.0						
ACRYLIC ACID	79-10-7	72.10	1.05	3.1	5.17E-07	1.00E-07	1.06E-05	9.80E-02	140.9	5.652	648.629	154.683			0.260
ACRYLONITRILE	107-13-1	53.06	0.81	114		8.80E-05	1.34E-05	1.22E-01	77.4	7.038	1232.53	222.47	7.0E-02	0.031	0.070
ADAMANTANE DICARBOXYLIC ACID	828-51-3	180.25		0.00076	2	9.01E-05									
ADAMANTANE DICHLORIDE		207.10			0.2	1.04E-03									
ADIPIC ACID	124-04-9	146.14	1.37	0.0000225		5.09E-11	6.84E-06	6.59E-02	265.0						
ALDICARB	116-06-3	190.29			6000	3.17E-08									
ALDRIN	309-00-2	364.93			0.01	3.65E-02									
ALLYL ALCOHOL	107-18-6	55.08	0.85	23.3	100000	1.80E-05	1.14E-05	2.64E-01	97.0						0.091
ALLYL CHLORIDE	107-05-1	76.53	0.94	368	100	3.71E-01			45.0						
ALPHA METHYL STYRENE	98-83-9	118.00	0.91	0.076	2	5.91E-03	1.14E-05	2.64E-01	165.4	6.923	1486.88	202.4			
ALPHA METHYL STYRENE DIMERS		236.00			2	1.18E-02									
ALPHA HYDROXYACETALDEHYDE		60		1520		9.50E-05									
ALPHA-HYDROXYADIPIMIDE		162.00			1000	1.62E-05									
AMINOBENZOIC ACID (-p)	150-13-0	137.15			3400	4.03E-06									
AMINOCYCLOHEXANE	108-91-8	99.18			100000	2.48E-04									
AMINOPHENOL (-o)	95-55-6	109.12		0.511	20000	3.07E-06	8.64E-06	7.74E-02	174.0						
AMINOPHENOL (-p)	101-80-4	109.12		0.833	6500	1.92E-05	2.39E-06	7.74E-02	164.0	-3.357	699.157	-331.343			
AMPHETAMINE	60-15-1	135.21			100	1.32E-04									
AMYL ACETATE (-n)	628-63-7	130.19	0.88	5.422		4.64E-04	1.20E-06	6.40E-02	148.4						0.130
ANILINE	62-53-3	93.10	1.02	1		2.60E-06	8.30E-06	7.00E-02	184.[illegible]	7.320	1731.515	206.049			0.560
ANISOLE	100-66-3	108.13		10	2	7.11E-01									
ANTHRACENE	120-12-7	178.23	1.25	1.30E-06		6.75E-02			340.0						

COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
ANTHRAQUINONE	84-65-1	208.20	1.43	3.00E-08		3.20E-09			380.0						
ARSANILIC ACID	98-50-0	217.04			2000	1.09E-07									
AZEPINE	111-49-9	93.20			10000	2.33E-03									
AZIRIDINE	151-56-4	43.10		160	20000	4.54E-04									
BAKELITE	9003-35-4	100000.00			0.2	5.00E-01									
BENZAL CHLORIDE	98-87-3	161.00	1.26	0.07	2	7.41E-03			207.0						
BENZALDEHYDE	100-52-7	106.13		1	3300	4.23E-05									
BENZALKONIUM CHLORIDE	8001-54-5	192.00			10000	1.93E-06									
BENZENE	71-43-2	78.10	0.87	95.2		5.50E-03	9.80E-06	8.80E-02	80.1	6.905	1211.033	220.790	1.2E-05		0.39
BENZENE SULFONIC ACID		158.17			20000	7.91E-07									
BENZETHONIUM CHLORIDE	121-54-0	448.15			2000	2.24E-05									
BENZO(A)ANTHRACENE	56-55-3	228.30	1.11	1.5E-07		1.38E-09	9.00E-06	5.10E-02	58.9				6.9E-06		
BENZO(A)PYRENE	50-32-8	252.30	1.11	5.68E-04		1.38E-09	9.00E-06	4.30E-02	312.0						
BENZO(B)FLUORANTHENE	205-99-2	252.32		1626		2.01E-05			4.0						
BENZODIOXANE-1,3		233.30			5000	4.67E-06									
BENZOIC ACID	65-85-0	122.13	1.27	0.00704		1.82E-08	7.97E-06		249.2	9.033	3333.3	273			0.84
BENZONITRILE	100-47-0	103.07		1	10000	1.36E-05									
BENZOPHENONE	119-61-9	182.23			2	9.11E-03									
BENZOTHIAZOLE	95-16-9	135.19			100	1.35E-04									
BENZOTRICHLORIDE	98-07-7	195.47	1.38	0.2		2.19E-03			221.0						
BENZOYL CHLORIDE	98-88-4	140.57		214											
BENZYL ALCOHOL	100-51-6	108.15		0.15	35000	6.10E-07									
BENZYL CHLORIDE	100-44-7	126.60	1.10	1.21		6.10E-03	7.80E-06	7.50E-02	179.4				1.2E-05	6.2	
BENZYL METHYL ETHER	538-86-3	122.16	0.987	0.076	10	1.22E-03									
BICYCLO(2.2.1)-2,5-HEPTADIENE DICHLORIDE		158.00			0.2	7.90E-02									
BIPHENYL	92-52-4	154.20	1.18	1	2	1.01E-01			254.0	7.245	1938.725	202.733			
BIS(1,1,2,2-TETRACHLOROPROPYL) ETHER		377.70		874.7	10	4.35E+01			21.3						
BIS(2-CHLOROETHYL)ETHER	111-44-4	143.00	1.22	1.4		1.30E-05	7.53E-06	6.93E-02	178.0				1.5E-05		
BIS(2-CHLOROISOPROPYL)ETHER	108-60-1	171.10	1.11	0.85		1.10E-04	6.41E-06	6.02E-02	189.0						
BIS(2-ETHYLHEXYL)PHTHALATE	117-81-7	390.68	0.99	2.0E-07		3.00E-07	3.66E-06	3.51E-02	384.0						
BIS(CHLOROMETHYL)ETHER	542-88-1	115.00	1.32	30		2.10E-04	9.38E-06	8.35E+01	104.0				2.7E-07		
BIS-DICHLOROPROPYL ETHERS		239.94			2	1.20E-02									
BISPHENOL (A)	80-05-7	228.31			10	2.28E-03									
BROMO-(1)-CHLOROETHANE-2	107-04-0	143.42			0.2	1.79E+02									
BROMOBENZENE	108-86-1	157.02	1.4952	0.076	450	3.49E-05									
BROMOBENZYL ALCOHOL -(m)	15852-73-0	187.04			5000	3.74E-06									
BROMOBENZYL ALCOHOL -(o)	18982-34-2	187.04			5000	3.74E-06									
BROMOBENZYL ALCOHOL -(p)	873-75-6	187.04			5000	3.74E-06									
BROMOCHLOROBENZYL ALCOHOL		205.00			2500	8.20E-06									
BROMOCHLOROMETHANE	74-97-5	129.39			10	2.53E+01									
BROMOCHLOROMETHYL ACETATE		187.00			100000	1.87E-07									
BROMODICHLOROMETHANE	75-27-4	163.80	1.97	50.15	200	2.05E-01			90.0						
BROMOETHYL ACETATE	927-68-4	167.02			100000	4.18E-06									
BROMOETHYLENE	593-60-2	106.96			2	1.34E+01									
BROMOFORM	75-25-2	252.77	2.89	5.6	3190	5.84E-04			149.5					20	
BROMOMETHANE	74-83-9	94.95	1.73	1250	900	2.21E-01			3.5						
BUTADIENE (1,3)	106-99-0	54.09	0.00	2095.045		1.43E-01	1.08E-05	2.49E-01	-4.4	6.849	930.546	238.854			
BUTANE	106-97-8	58.12			400	2.91E-01									
BUTANOL (S)	78-92-2	74.14		10	77000	1.27E-05									
BUTANOL 1	71-36-3	74.12	0.81	6.5		8.91E-06	9.30E-06	9.00E-02	117.7	7.476	1362.39	178.77			0.42
BUTYL ACETATE (n)	123-86-4	116.00	0.88	15	14000	1.64E-04			125.0	7.127	1430.418	210.745			0.07

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BUTYL ACRYLATE	141-32-2	128.20	0.90	5.8	1600	6.11E-04			145.0						
BUTYL BENZENE	104-51-8	134.22		1	2	8.83E-02									
BUTYL BENZYL PHTHALATE	85-68-7	312.39			2.9	1.08E-02									
BUTYL CARBITOL	112-34-5	162.23	0.96	4.60E-03	0.2	8.11E-02			231.0						
BUTYL CELLOSOLVE	111-76-2	118.20	0.90	1.61	45000	2.63E-07			170.0	6.956	1399.903	172.154			
BUTYL MERCAPTAN	109-79-5	90.19			100	2.25E-01									
BUTYLENE GLYCOL -(1,3)	107-88-0	90.14		0.06	2000	3.56E-06									
BUTYRALDEHYDE	123-72-8	72.11			70000	2.50E-04									
BUTYRIC ACID	107-92-6	88.10		0.84	56200	1.73E-06									
CAMPHENE	79-92-5	136.26	0.84		10	1.36E-03			159.0						
CARBAZOLE	86-74-8	167.20		1	2	4.40E+01									
CARBON DISULFIDE	75-15-0	76.14	1.26	366		1.68E-02			46.3	6.942	1169.11	241.59			
CARBON OXYFLUORIDE	353-50-4	65.01		1520	100000	1.32E-03									
CARBON TETRACHLORIDE	56-23-5	153.80	1.59	113		3.00E-02	8.80E-06	7.80E-02	76.8	6.93390	1242.43	230	1.5E-05		
CELLULOSE	9000-11-7	594.27			10	5.94E-05									
CHLORAL	302-17-0	147.40	1.51	50	10000	9.70E-04			97.6						
CHLORDANE	57-74-9	410.00	1.11	1.0E-05		3.67E-05							1.0E-05		
CHLORINATED TARS		350.00			12	1.75E-04									
CHLORINE	7782-50-5	35.45		4800	3200	7.00E-02									
CHLORO(-3)PROPENE-1	557-95-2	75.60		361	100	3.59E-01									
CHLORO(-p)CRESOL(-m)	59-50-7	142.60		3.50E-03	4000	1.64E-07			235.0						
CHLORO(-p)PHENYLHYDRAZINE		142.00			50	2.84E-04									
CHLORO-1,2 ETHANE DIOL		96.52			100000	9.65E-08									
CHLORO-p-XYLENE	104-82-5	140.61		60	10	1.11E+00									
CHLOROACETALDEHYDE	107-20-0	78.50	1.11	60		2.60E-05	1.15E-05	9.90E-02	85.0					0.38	
CHLOROACETIC ACID	79-11-8	94.50		1	850000	1.11E-08									
CHLOROANILINE(2)	95-51-2	127.60		1	10	1.68E-02									
CHLOROANILINE(3)	108-42-9	127.57		1	10	1.68E-02									
CHLOROAZOBENZENE		216.70			2	1.08E-02									
CHLOROBENZENE	108-90-7	112.56	1.11	11.8		3.93E-03	8.70E-06	7.30E-02	132.0	6.978	1431.05	217.55	2.7E-03	50	0.15
CHLOROBENZENESULFONIC ACID (-p)	100-03-8	176.62			2000	8.83E-06									
CHLOROBENZOIC ACID (-o)	118-91-2	156.57			2100	7.46E-06									
CHLOROBENZOPHENONE (PARA)	134-85-0	216.67		2.60E-06		3.40E-09			330.0						
CHLOROBENZYL ALCOHOL -(m)	873-63-2	142.59			5000	2.85E-06									
CHLOROBENZYL ALCOHOL -(o)	17849-38-6	142.59			5000	2.85E-06									
CHLOROBENZYL ALCOHOL -(p)	873-76-7	142.59			5000	2.65E-06									
CHLORODIPHENYL (-p)		188.00			2	9.40E-03									
CHLOROCYANOBENZENE (1,4)	873-32-5	137.50			2	1.72E+01									
CHLOROCYCLOHEXANE	542-18-7	118.51			2	1.48E+01									
CHLORODIACETYL		120.5		190	10000	3.01E-03									
CHLOROETHANE	75-00-3	64.52	0.92	1200		9.10E-03	1.15E-05	2.71E-01	12.5	6.986	1030.01	238.61			
CHLOROETHYL(2-) VINYL ETHER	110-75-8	106.55		24.7	100	3.46E-02			109.0						
CHLOROFLUOROMETHANE	593-70-4	68.48			10	1.71E+00									
CHLOROFORM	67-66-3	119.40	1.49	208		3.39E-03	1.00E-05	1.04E-01	61.7	6.493	929.44	196.03	1.0E-05		
CHLOROMETHANE	74-87-3	50.49	0.95	3830	8000	8.14E-03									
CHLOROMETHYL ACETYLENE		74.5		190	10	1.06E+00									
CHLOROMETHYL ETHYL KETONE		106.55			10000	2.66E-03									
CHLOROMETHYL PHENYL KETONE	532-27-4	154.60			5000	2.09E-06									
CHLOROMETHYLAMINOIMINE		78.5		0.076	2000	3.93E-06									
CHLORONAPHTHALENE-2	91-58-7	162.51		0.017	0.2	1.85E-02			256.0						
CHLORONITROSOXYIMINE		[illegible]			1000	2.30E-05									

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CHLORONITROBENZENE(-o)	89-73-3	157.56			2	7.88E-03									
CHLOROPHENOL POLYMERS		2000.00			20000	1.00E-07									
CHLOROPHENOL-2	95-97-8	128.60	1.26	3	28500	1.78E-05			175.6	6.877	1471.61	193.17			
CHLOROPHENOL-3	108-43-0	128.60	1.24	0.5	28000	3.25E-06			214.0						
CHLOROPHENOL-4	106-48-9	128.60	1.31	0.18	27100	1.12E-06			217.0						
CHLOROPRENE	126-99-8	88.50	0.96	273	100	3.35E-01		1.03E-01	59.4	6.161	783.45	179.7			
CHLOROPROPANE-1	540-54-5	78.54	0.89	350		1.30E-02			47.2						
CHLOROPROPANE-2	75-29-6	78.54	0.87	523		1.70E-02			36.5						
CHLOROPROPYLENE-2	557-98-2	75.60		361	100	3.59E-01									
CHLOROSTYRENE (-4)	1331-28-8	138.60			2	6.93E-03									
CHLOROTOLUENE-4	106-43-4	126.60	1.07	2.8	100	4.66E-03			162.0						
CHRYSENE	218-01-9	228.20	1.11	5.76E-10		1.18E-09			488.0						
CITRIC ACID	77-92-9	192.12	1.665	0.001	400000	6.32E-10									
COPPER PHTHALOCYANINE	147-14-8	576.10			10	5.76E-03									
COUMARAN	91-64-5	146.15		1	2	9.62E-02									
CREOSOTE	8001-58-9	400.00			5000	8.00E-08									
CRESOL	1319-77-3	108.13	1.03	0.3	2000	2.55E-06	0.00001	0.074						395	0.57
CRESOL(-m)	108-39-4	108.13	1.03	0.08		4.43E-07			203.0	7.508	1855.36	199.07		395	0.708
CRESOL(-o)	95-48-7	108.13	1.04	0.24		2.60E-06	8.30E-06	7.40E-02	190.8	6.911	1435.50	165.16			
CRESOL(-p)	106-44-5	108.13	1.03	0.11		4.43E-07			202.0	7.035	1511.08	161.85			
CROTONALDEHYDE	470-30-3	70.09	0.85	30		1.54E-05	1.02E-05	9.03E-02	99.0					6.9	0.58
CROTONYLENE	503-17-3	54.09			2	6.76E+00									
CUMENE (isopropylbenzene)	98-82-8	120.20	0.86	4.6		1.46E-02	7.10E-06	6.50E-02	153.0	6.963	1460.793	207.78			
CUMYLPHENOL-4	27576-86-9	212.29	0.00	0.000012	2	1.68E-06			335.0						
CYANOGUANIDINE	461-58-5	84.08		0.076	10000.	8.41E-07									
CYANOPYRIDINE (-4)	100-48-1	104.11			100	2.60E-01	8.78E-06	7.98E-02	195.4						
CYANURIC ACID	108-80-5	129.09			5000	2.58E-06									
CYCLOHEXANE	110-82-7	84.20	0.78	100		1.37E-02	9.10E-06	8.39E-02	81.0	6.841	1201.53	222.65			
CYCLOHEXANOL	108-93-0	100.20	0.95	1.22		4.47E-06	8.31E-06	2.14E-01	161.0	6.255	912.87	109.13			
CYCLOHEXANONE	108-94-1	98.15	0.95	4.8		4.13E-06	8.62E-06	7.84E-02	157.0						
CYCLOHEXENE	110-83-8	82.15				1.03E+01									
CYCLOHEXYL ACETATE	622-45-7	142.22			200	7.11E-05									
CYCLOPENTADIENE	542-92-7	66.10	0.82	4	2	1.93E+01			40.0						
DACRON		100000.00			0.2	5.00E-01									
DDT	50-29-3	354.49			0.0031	1.14E-01									
DI n-OCTYL PHTHALATE	117-84-0	390.62			0.285	1.37E-01									
DIACETYL	431-03-8	86.10			250000	8.61E-05									
DIBENZO(A,H)ANTHRACENE	53-70-3	278.36		5.200E-11		3.81E-08									
DIBROMOCHLOROMETHANE	124-48-1	208.29	2.38		0.2	2.08E+03			122.0						
DIBROMOETHANE-1,2	106-93-4	187.88			4310	1.09E-02									
DIBROMOMETHANE	74-95-3	173.85		48	11000	9.98E-04									
DIBUTYL ETHER	142-96-1	130.22	0.87	7	300	4.00E-03									
DIBUTYLPHTHALATE	84-74-2	278.30	1.47	0.00001		2.80E-07	7.86E-06	4.38E-02	340.0	6.639	1744.20	113.59			0.2
DICHLORO(1,3)PROPANOL(-2)	96-23-1	129.00	1.35	0.27	100000	4.60E-06			82.0						
DICHLORO(2,3)PROPANOL(-1)	616-23-9	129.00	1.35	7		2.34E-05			182.0						
DICHLORO-(2,6)-NITROANILINE(4)	99-30-9	206.98		0.0000012	50	6.54E-03									
DICHLORO-2-BUTENE(1,4)	764-41-0	125.00	1.19	2.87		2.59E-04	8.12E-06	7.25E-02	158.0						
DICHLORO-TRANS-ETHYLENE(1,2)	540-59-0	96.94		400	600	8.50E-02									
DICHLOROBENZENE(1,2) (-o)	95-50-1	147.00	1.31	1.5		1.94E-03	7.90E-06	6.90E-02	179.0					320	
DICHLOROBENZENE(1,3) (-m)	541-73-1	147.00	1.29	2.28		3.61E-03	7.86E-06	6.92E-02	172.0						
DICHLOROBENZENE(1,4) (-p)	106-46-7	147.00	1.46	1.2		1.60E-03	7.90E-06	6.90E-02	173.4						

COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
DICHLOROBIPHENYL (PARA)	213029-08-8	223.10			0.62	3.60E-02	5.84E-06	5.30E-02						375	
DICHLOROBUTANE (1,4)	110-56-5	127.01			10	3.18E+00									
DICHLORODIFLUOROMETHANE	75-71-8	120.92	1.49	5000		4.01E-01	1.00E-05	1.04E-04							
DICHLORODIPHENYLMETHANE	2051-90-3	237.00			2	1.19E-02									
DICHLOROETHANE (1,1)	75-34-3	99.00	1.17	234	5500	5.54E-03			57.0						
DICHLOROETHANE (1,2)	107-06-2	98.76	1.26	82		1.20E-03	9.90E-06	1.04E-01	83.5	7.025	1272.3	222.9	6.6E-03		0.002
DICHLOROETHYLENE (1,1)	75-35-4	97.00	1.21	630.1		1.50E-02			-99.8						
DICHLOROETHYLENE (1,2)	156-54-2	96.95	1.28	200	800	3.19E-02			60.0	6.965	1141.9	231.9	6.1E-06		
DICHLOROMETHANE	75-09-2	85.00	1.34	438		3.19E-03	1.17E-05	1.04E-01	39.8	7.409	1325.9	252.6	1.8E-07	650	
DICHLOROMONOFLUOROMETHANE	75-43-4	102.92		1360	0.2	9.21E+02			9.0						
DICHLOROPHENOL (2,4)	120-83-2	163.01		0.1		4.80E-06			210.0						
DICHLOROPHENOL (2,6)	87-65-0	163.00		0.034		4.80E-06			220.0						
DICHLOROPHENOXYACETIC ACID(2,4)	94-75-7	221.04		289.5	890	6.21E-02	6.49E-06	5.88E-02	47.2						
DICHLOROPROPANE (1,2)	78-87-5	112.99	1.16	40		2.30E-03	8.73E-06	7.82E-02	96.8	6.980	1380.1	22.8			
DICHLOROPROPENE (1,3)	542-75-6	111.00	1.20	43	2700	2.33E-03			112.0						
DICHLOROPROPYLENE-2,3	78-88-6	110.97			2150	1.29E-02									
DIETHYL (N,N) ANILINE	91-66-7	149.23	0.93	0.002825	14400	5.74E-08	5.87E-06	5.13E-02	298.0						
DIETHYL AMINE	109-89-7	73.14			20000	7.31E-03									
DIETHYL ETHER	602-97-6	74.12	0.71		69900	2.65E-04	8.61E-06	7.82E-02	34.5	7.636	1939.4	162.7			
DIETHYL ETHER ACID CHLORIDE		136.5		0.076	100	1.37E-04									
DIETHYL PHTHALATE	84-66-2	222.00	1.12		2	1.11E-02									
DIETHYL THIOETHER	352-93-2	90.00			50	4.50E-01									
DIETHYLENE GLYCOL	111-46-6	106.14		1	100000	1.40E-06									
DIHYDRO-5-OXAZALONE (DIHYDROAZLACTONE)		101		0.076	5000	2.02E-06									
DIISOPROPYL BENZENE (PARA)	100-18-5	162.28		1	2	1.07E-01									
DIMETHOATE	60-51-5	229.27			25000	9.17E-07									
DIMETHOXY METHANE	109-87-5	76.10		400	330000	1.21E-04									
DIMETHOXY-(3,3') BENZIDINE	119-90-4	244.32			10	2.44E-03									
DIMETHYL AMINE	124-40-3	45.09		1520	20000	5.24E-06									
DIMETHYL DISULFIDE	624-92-0	94.20			6300	1.50E-06									
DIMETHYL FORMAMIDE	68-12-2	73.09	0.95	3.995	20000	1.92E-05	1.03E-05	9.39E-02	152.8	6.928	1400.87	196.43			
DIMETHYL HYDRAZINE (1,1)	57-14-7	60.10	0.80	157	100000	1.24E-04	1.09E-05	1.06E-01	63.0	7.408	1305.91	225.53			
DIMETHYL NITROSAMINE	62-75-9	74.08	1.005				0.00001	0.104	153						
DIMETHYL PHTHALATE	131-11-3	194.20	1.19	0.000187		2.15E-06	6.29E-06	5.68E-02	283.8	4.522	700.31	51.42			
DIMETHYL SULFATE	77-78-1	126.14		0.1		5.86E-07									
DIMETHYL SULFIDE	75-18-3	62.12		420	6300	5.45E-03									
DIMETHYLBENZ(A)ANTHRACENE (7,12)	57-97-6	256.33		1.62E-09	2	2.73E-10	4.98E-06	4.61E-02	477.0						
DIMETHYLBENZYL HYDROPEROXIDE	80-15-9	152.21		0.24	100	4.81E-04									
DIMETHYLETHYLAMINE	75-64-9	73.19	1.11	20	5000	3.85E-04									
DIMETHYLPHENOL (2,4)	105-67-9	122.16	1.04	0.0573	10	9.21E-04			211.5						
DINITRO o-CRESOL (4,6)	534-52-1	198.00		0.018		1.40E-05			254.[illegible]						
DINITROBENZENE (-m)	99-65-0	169.10	1.56	0.05		2.20E-05	7.64E-06	2.79E-01	300.0	4.337	229.2	-137			
DINITROPHENOL (2,4)	51-28-5	184.00	1.68	53.8		1.53E-07			83.[illegible]						
DINITROTOLUENE (2,4)	121-14-2	182.10	1.31	0.0051		4.07E-06	7.06E-06	2.03E-01	300.0	5.799	1118	61.8			
DINOCAP	39300-45-3	364.40		.001	2	1.96E+05			-168.7						
DIOXANE (1,4)	123-91-1	98.20	1.03	37		2.31E-05	1.02E-05	2.29E-01	101.0	7.431	1554.68	240.34			
DIOXIN	[illegible]	459.70		1.00E-09	3.000E-11	2.03E+01									
DIOXIN	[illegible]	322.00		1.00E-09	3.000E-11	1.41E+01			106.6						
DIPHENYL ETHER	101-84-8	170.21	1.075	0.02	2	2.24E-03									
DIPHENYL OXIDE															
DIPHENYL THIOETHER	139-66-2	186.28			2	9.31E-03									

COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	PDI in AIR (g/m3)	BOD/COD RATIO
DIPHENYLAMINE	122-39-4	169.20	1.16	0.00375		2.78E-06	6.31E-06	5.80E-02	302.0						
DIPHENYLCHLOROMETHANE	90-99-3	202.00			2	1.01E-02									
DIPHENYL DIKETONE	134-81-6	210.24			2	1.05E-02									
DIPHENYLHYDRAZINE(1,2)	122-66-7	184.23		0.0000523		1.00E-10			220.0						
DIPHENYLMETHANE	101-81-5	168.20		1	3	7.38E-02									
DIPROPYLAMINE	142-84-7	101.22			100000	2.53E-04									
DIVINYL KETONE		70.00			40000	4.38E-04									
ENSODULFAN	115-29-7	406.95		0.00076	10	4.07E-05									
EPICHLOROHYDRIN	106-89-8	92.50	1.18	17		3.23E-05	9.80E-06	8.60E-02	117.0				2.2E-07		
EPINEPHRINE	51-43-4	183.21			500	3.66E-07									
ETHANOL	64-17-5	46.10	0.79	50	100000	3.03E-05	1.30E-05	1.23E-01	78.4	8.321	1718.21	237.52			
ETHANOLAMINE(mono-)	141-43-5	61.09	1.02	0.4	100000	3.22E-07	1.14E-05	1.07E-01	172.0	7.456	1577.67	173.37			0.46
ETHOXYETHANOL-2	110-80-5	90.00	0.90	5.4	100000	6.39E-06			135.0	7.874	1843.5	234.2			0.09
ETHYL ACETATE	141-78-6	88.10	0.9	100		1.28E-04	0.00000366	0.0723	77	7.101	1244.95	217.88			0.36
ETHYL ACETATE PEROXIDE		120.00			10000	3.06E-03									
ETHYL ACRYLATE	140-88-5	100.00	0.92	40		3.50E-04	8.60E-06	7.70E-02	100.0						
ETHYL BENZENE	100-41-4	106.16	0.86	10		6.44E-03	7.80E-06	7.50E-02	136.2	6.975	1424.255	213.21			0.003
ETHYL CHLORIDE	75-00-3	64.52	0.92	1200		9.10E-03	1.15E-05	2.71E-01	12.5	6.986	1030.01	238.61			
ETHYL CYANIDE	107-12-0	55.08		40	50000	2.75E-04									
ETHYL ETHER	60-29-7	74.12	0.71	520		6.80E-04	9.30E-06	7.40E-02	34.5	6.920	1064.07	228.8			0.012
ETHYL ISOPROPYL PEROXIDE		104.00			100000	2.60E-04									
ETHYL (2) HEXANOL	104-76-7	130.22		0.36	1000	6.17E-05									
ETHYL-(2)-PROPYL-(3) ACROLEIN	645-62-5	92.50	1.18	17		3.23E-05	9.80E-06	8.60E-02	117.0				1.2E-06		
ETHYLENE	74-85-1	28.95			131	4.42E-01									
ETHYLENE CHLOROHYDRIN	107-07-3	80.52		10	100000	1.06E-05									
ETHYLENE DIAMINE	107-15-3	60.11		10.7	100000	8.46E-06									
ETHYLENE DIBROMIDE	106-93-4	187.88	2.70	14	4310	1.09E-02			131.6	6.721	1280.82	201.75			
ETHYLENE DICHLORIDE	107-06-2	98.76	1.25	82		1.20E-03	9.90E-06	1.04E-01	83.5	7.025	1272.3	222.9	6.6E-03		0.002
ETHYLENE GLYCOL	107-21-1	62.07	1.11	0.1256	100000	1.03E-07	1.22E-05	1.08E-01	198.0	8.090	2088.9	203.5			0.081
ETHYLENE GLYCOL DIMETHYL ETHER	110-71-4	90.12		48	100000	5.69E-05									
ETHYLENE GLYCOL MONOMETHYL ETHER	109-86-4	76.10		0.76	100000	7.61E-07									
ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE	110-49-6	118.15		2	100000	3.11E-06									
ETHYLENE OXIDE	75-21-8	44.00	0.87	1250		1.42E-04	1.00E-05	1.04E-01	10.7	7.128	1054.54	237.76			
FLUORANTHENE	206-44-0	202.00		0.0177	0.3	6.73E-02			250.0	6.373	1755	118			
FLUORENE	86-73-7	166.00	1.20	0.0000163	2	1.78E-06			293.0	7.761	2637.1	243.2			
FLUOROACETIC ACID, SODIUM SALT	62-74-8	100.02			20000	5.00E-09									
FORMALDEHYDE	50-00-0	30.00	1.08	3500		5.76E-05	1.98E-05	7.40E-02	-19.0	7.195	970.6	244.1	9.0E-04		0.35
FORMIC ACID	64-18-6	46.00	1.22	42		7.00E-07	1.37E-06	7.90E-02	100.7	7.581	1699.2	260.7			0.05
FUMARIC ACID	110-17-8	116.07			7000	1.66E-06									
FURAN	110-00-9	68.08	0.94	596.207		5.34E-03	1.22E-05	1.04E-01	31.4	6.975	1060.87	227.74			
FURFURAL	98-01-1	96.09	1.16	2		8.11E-05	1.04E-05	8.72E-02	161.7	6.575	1198.7	162.8			0.17
FUROIC ACID	88-14-2	112.08		190	38000	7.37E-04									
GLUTARIC ACID	110-94-1	132.11			640000	2.06E-08									
GLYCERIN	56-81-5	92.09	1.25	0.00016	10000	1.94E-09			291.0						
GLYCEROL	56-81-5	92.10	1.25	0.00016	10000	1.94E-09			291.0						
GLYCINAMIDE	598-41-4	74.08			50000	1.49E-07									
GUANIDINE, NITROSO	674-81-7	88.09			10000	8.21E-07									
GLYCIDOL	556-52-5	74.08	1.11	0.925	100000	9.02E-07			162.0						
HEAVY CHLORINATED ORGANICS		200.00			0.2	1.50E-01									
HEPTACHLOR	76-44-8	373.35	1.57	0.0003		2.3[illegible]E-03			[illegible]						
HEPTANE(-n)	142-82-5	100.20	0.68	46	3	2.03E+00			98.4	6.896	1264.9	216.54			

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HEXACHLOROBENZENE	118-74-1	284.80	2.04	1		6.80E-04	5.91E-06	5.42E-02	322.0						
HEXACHLOROBUTADIENE	87-68-3	260.76	1.67	0.15		2.56E-02	6.16E-06	5.61E-02	215.0						
HEXACHLOROCYCLOHEXANE (GAMMA ISOMER)	58-89-9	290.83	1.87	9.40E-06	17	7.80E-06									
HEXACHLOROCYCLOPENTADIENE	77-47-4	272.77	1.71	0.081		1.60E-02	6.16E-06	5.61E-02	239.0					1.8	
HEXACHLOROETHANE	67-72-1	237.00	2.09	0.65		2.49E-06	6.80E-06	2.49E-03	186.0						
HEXACHLOROPENTADIENE		275.00			2	1.38E-02									
HEXANE(-n)	110-54-3	86.20	0.66	150.3		1.22E-01	7.77E-06	2.00E-01	69.0	6.876	1171.17	224.41			
HEXANOIC ACID	142-62-1	116.06			11000	1.06E-06									
HEXANOL-1	111-27-3	102.18	0.82	0.8115		1.82E-05	7.53E-06	5.90E-02	158.0	7.860	1761.26	196.66			0.2
HYDRAZINE	302-01-2	32.06		14.4		6.66E-07									
HYDROQUINONE	123-31-9	110.12			70000	1.57E-07									
HYDROXY DIMETHYL ETHER		78.00			1000	1.95E-02									
HYDROXY-(2)-PROPIONITRILE	109-78-4	71.09		0.08	100000	7.48E-08									
HYDROXYACETIC ACID	79-14-1	76.05			100000	1.90E-04									
HYDROXYMETHYL ACETYLENE		56		190	10	1.40E+00									
HYDROXYMETHYL ISOPROPYL KETONE		90.00			10000	2.25E-03									
HYDROXYMETHYLTHIOBENZENE		140.00			2	7.00E-03									
HYDROXYMETHYLVINYL ETHER		130.00			1000	3.25E-02									
INDENO(1,2,3-cd)-PYRENE	193-39-5	276.34				5.07E-13			536.0						
ISOBUTYL ALCOHOL(ISOBUTANOL)	78-83-1	74.12	0.80	10		2.20E-06	9.30E-06	8.60E-02	107.9						0.63
ISOBUTYRALDEHYDE	78-84-2	72.12		170	110000	1.47E-04									
ISOHEPTANE	31394-54-4	100.21	0.68	65.97	2	4.35E+00	7.11E-06	1.87E-01	90.0						
ISOPHORONE	78-59-1	138.21	0.92	0.439		5.76E-06	6.76E-06	6.23E-02	215.0						
ISOPROPANOL	67-63-0	60.09	0.79	42.8	100000	1.50E-04	1.04E-05	9.80E-02	82.4	8.117	1580.92	219.61			0.56
ISOPROPYL ACETATE	108-21-4	102.13		73	30900	3.17E-04									
ISOPROPYL ETHER	108-20-3	102.18		150	9000	2.24E-03									
ISOPROPYLAMINE	75-31-0	59.08		460	100000	3.50E-04									
LEUCINE	61-90-5	131.20			24300	5.40E-07									
MALEIC ACID	110-16-7	116.07			788000	1.47E-09									
MALEIC ANHYDRIDE	108-31-6	98.10	0.93	0.0001	788	4.00E-08	1.11E-05	9.50E-02	200.0						0.51
MALONONITRILE	109-77-3	66.06		0.000569	20000	2.47E-09									
MELAMINE	108-78-1	126.20		50	100	8.30E-02									
MESITYL OXIDE	141-79-7	98.15			28000	3.51E-07									
METHACRYLIC ACID	79-41-4	86.10		0.1	1000	1.13E-05									
METHANE	74-82-8	16.04			24	1.34E+00									
METHANE SULFONIC ACID	75-75-2	96.11			20000	4.81E-07									
METHANETHIOL	74-93-1	48.11		1520	23000	4.18E-03									
METHANOL	67-56-1	32.04	0.79	114		2.70E-06	1.64E-05	1.50E-01	65.0	7.897	1474.08	229.13			0.07
METHOMYL	16752-77-5	162.20			20000	8.11E-07									
METHOXYACETIC ACID		90.00			5000	1.80E-05									
METHOXYACETONITRILE	1738-36-9	71.04			100000	1.79E-04									
METHYL 1-[(BUTYLAMINO) CARBONYL]-1H-BENZIMIDAZOL-2-		250.00 E			2	1.25E-02									
METHYL ACETATE	79-20-9	74.10	0.92	235	2000	1.15E-02	1.00E-05	1.04E-01	54.0	7.065	1157.63	219.73			
METHYL ACRYLATE	96-33-3	86.10			60000	1.44E-07									
METHYL CHLORIDE	74-87-3	50.50	0.95	3830	8000	8.14E-03	6.50E-05	1.26E-01	-24.0	7.093	948.58	249.34	1.4E-07		
METHYL CHLOROCARBONATE	79-22-1	94.50			100	2.30E-01									
METHYL CYCLOHEXANE	108-87-2	98		43	2	2.71E+00									
METHYL ETHER	115-10-6	46.09		3982	76000	3.18E-03									
METHYL ETHYL KETONE	78-93-3	72.12	0.82	100		4.35E-05	9.80E-06	8.09E-02	79.6	6.97421	1209.6	216.0		70	0.88
METHYL FORMATE	107-31-3	60.06		500	300	1.30E-01									
METHYL HYDRAZINE	60-34-4	46.03		49.6		3.66E-06									

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METHYL IODIDE	74-88-4	141.94			14000	2.53E-03									
METHYL ISOAMYL KETONE	110-12-3	114.00	0.80	4.53	5400	1.26E-04			144.0						
METHYL ISOBUTYL KETONE	108-10-1	100.16	0.80	15.7	19000	4.95E-05	7.80E-06	7.50E-02	115.8	6.672	1169.4	191.9		365	0.044
METHYL ISOCYANATE	624-83-9	57.06			dec.										
METHYL ISOPROPYL KETONE	563-80-4	86.15			47000	4.58E-04									
METHYL METHACRYLATE	80-62-6	100.10	0.95	39		6.60E-05	8.60E-06	7.70E-02	101.0	8.409	2050.5	274.4			0.24
METHYL NAPTHALENE(1-)	90-12-0	142.19		0.1		7.10E-04			241.5						
METHYL NAPTHALENE(2-)	91-57-6	142.19		0.0083	2	5.80E-05			241.5						
METHYL SULFURIC ACID		112.10			20000	5.61E-07									
METHYL(A)STYRENE DIMERS	6144-04-3	236.18			2	1.18E-02									
METHYL-2-AMINOETHYLAMINE	109-81-9	74.05			1000	1.85E-02									
METHYL-2-HYDROXYETHYLAMINE	109-83-1	75.11		0.7	20000	3.46E-06									
METHYLACRYLONITRILE	126-98-7	67.09		65	25	3.92E-01	9.90E-06	9.10E-02		6.980	1274.95	220.7		0.2	
METHYLAMINE	74-89-5	31.06		1520	11539	5.38E-03									
METHYLAMINOACETYLENE		54.00			100	1.35E-01									
METHYLBIPHENYL (-p)	644-08-6	168.45			2	8.43E-03									
METHYLENE CHLORIDE	75-09-2	85.00	1.34	438		3.19E-03	1.17E-05	1.04E-01	39.8	7.409	1325.9	252.6	1.8E-07	650	
METHYLENEDICHLORIDE	75-09-2														
METHYLIMINOACETIC ACID		100.00			10000	1.00E-06									
METHYLSULFURIC ACID		112.1		0.076	100000	1.12E-07									
METHYLTIN TRICHLORIDE	993-16-8	240.08			100	2.40E-06									
MONOCHLORODIFLUOROMETHANE	75-45-6	86.50		7483	2	4.26E+02			-40.8						
MORPHOLINE	110-91-8	87.12	1.00	10	20000	5.73E-05	9.60E-06	9.10E-02	129.0						0.004
MCMA	2163-80-6	161.96			500	3.24E-07									
N,N-DIMETHYL BENZYLAMINE	103-83-3	135.23			10	1.35E-03									
N,N-DIMETHYL METHYLTHIOCARBAMATE		119		0.076	2000	5.95E-06									
N,N-DIMETHYL NITROISOPROPYLAMINE		133.00			50	2.66E-04									
N-HYDROXYMETHYL, N-METHYLETHYL AMINE		89.00			50	4.45E-01									
N-HYDROXYMETHYLPHENYL CARBAMATE		156.00			1000	1.56E-05									
N-METHYL, N-PHENYLETHYLAMINE	589-08-2	135.23			10	1.35E-03									
N-METHYL-2,3,4-TRIHYDROQUINOLINE		146.00			1000	1.46E-05									
N-METHYLCHLOROACETAMIDE		107.50			1000	1.08E-05									
N-METHYLPHENYL CARBAMATE		140.00			1000	1.40E-05									
N-NITROSO-N-METHYLUREA	684-93-5	103.10			2	5.16E-05									
N-NITROSOPYRROLIDINE	930-55-2	100.12			2	1.25E+01									
N-SUBST-ALKYLAMINE CARBOXYLIC ACID		200.00			2000	1.00E-05									
NAPHTHALENE	91-20-3	128.20	1.14			1.18E-03	7.50E-06	5.90E-02	218.0	7.010	1733.71	201.86		900	
NAPHTHOQUINONE-1,4	130-15-4	158.00	1.42	0.11111	1000	2.31E-05		0.00E+00	100.0						
NEOPENTYL GLYCOL	126-30-7	104.17			650000	1.60E-08									
NEOPRENE	9010-98-4	100000.00	1.23	0.001	2				59.4						
NIACIN	59-67-6	123.12			20000	6.16E-07									
NIACINAMIDE	98-92-0	122.14			10000	1.22E-06									
NITROANILINE(-o)	88-74-4	138.14	1.44	0.003		5.00E-07	8.00E-06	7.30E-02	284.1	8.868	3325.50	0			
NITROBENZENE	98-95-3	123.11	1.20	0.3		1.31E-05	8.60E-06	7.60E-02	210.8	7.115	1746.6	201.8	1.2E-03	200	
NITROCELLULOSE	9004-70-0	10000.00			10	1.00E-03									
NITROGLYCERIN	55-63-0	227.09	1.60	0.0036		6.60E-19			260.0						
NITROMETHANE	75-52-5	61.05		27.9	95	2.35E-02									
NITROPHENOL(4)	100-02-7	139.00	1.40	0.555	16	6.34E-03			279.0						
NITROSOMORPHOLINE		116.14					0.00001	0.059	225						
NITROTOLUENE (-p)	99-99-0	137.13		1	442	4.[illegible]E-04									
O,O DIETHYL O-2-ETHYLTHIOETHYL PHOSPHORO	126-75-0	258.36		1.300E-13	2	2.21E-14			549.5						

COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
O-CHLORONITROBENZENE	88-73-3	157.56			2	7.89E-03									
O-ETHYL S,S-DIPHENYL PHOSPHORODITHIOATE	1709-49-8	310.38			2	1.55E-04									
O-POLYCYCLIC KETO		1000.00			2	5.00E-02									
O-XYLYL CHLORIDE	552-45-4	140.60			10	1.41E-03									
OCTANE	111-65-9	114.30	0.70	17	0.66	3.87E+00			125.7	6.918	1351.99	209.15			
OCTYL ALCOHOL	111-87-5	130.30		0.124	300	4.34E-05									
ORGANIC OILS PIGMENTS		300.00			2	1.50E-04									
OXALIC ACID	144-62-7	90.04			20000	4.50E-09									
OXAMIC ACID	471-47-6	89.03	89.1		100	8.90E-05									
P,P'-DIAMINODIPHENYLMETHANE	101-77-9	198.26		0.076	100	1.90E-04									
PARA-BROMOCHLOROBENZENE	106-39-8	191.46			0.2	2.39E+02									
PARA-CHLOROFLUOROBENZENE	352-33-0	130.00			0.2	1.63E+02									
PARA-CHLOROTHIOPHENOL	106-54-7	144.62			0.2	7.23E-02									
PARA NITROANILINE	100-01-6	138.14		1	800	2.27E-04									
PARA-XYLYL CHLORIDE	104-82-5	140.61		60	10	1.11E+00									
PARAFORMALDEHYDE	30525-89-4	1000.00			100	1.00E-03									
PARALDEHYDE	123-63-7	132.30	0.99	25.3	120000	3.67E-05			125.0						
PARATHION	56-38-2	291.30	1.26	0.003		4.80E-05			375.0						
PCB-1254	11097-69-1	225.10	1.11	0.00008	0.08	2.96E-04									
PENTACHLOROBENZENE	608-93-5	250.34	1.61	0.0046		7.30E-03	6.30E-06	5.70E-02	277.0						
PENTACHLOROETHANE	76-01-7	202.30	1.67	4.4		2.10E-02	7.30E-06	6.60E-02	162.0	6.740	1378	197	2.2E-02		
PENTACHLOROPHENOL	87-86-5	266.40	1.98	0.00099		2.80E-06	6.10E-06	5.60E-02	310.0				3.9E-07		
PENTAERYTHRITOL	115-77-5	136.15		0.076	55000	2.48E-07									
PENTAERYTHRITOL TETRANITRATE	78-11-5	316.17			10	3.16E-05									

KEY	COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS			UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
											A	B	C			
515	OCTYL ALCOHOL	111-87-5	130.30		0.124	300	4.34E-05									
892	ORGANIC OILS PIGMENTS	892	300.00			2	1.50E-04									
776	OXALIC ACID	144-62-7	90.04			20000	4.50E-09									
90	OXAMIC ACID	471-47-6	89.03	89.1		100	8.90E-05									
952	P,P'-DIAMINODIPHENYLMETHANE	101-77-9	198.26		0.076	100	1.98E-04									
140	PARA-BROMOCHLOROBENZENE	106-39-8	191.46			0.2	2.39E+02									
142	PARA-CHLOROFLUOROBENZENE	352-33-0	130.00			0.2	1.63E+02									
145	PARA-CHLOROTHIOPHENOL	106-54-7	144.62			0.2	7.23E-02									
522	PARA-NITROANILINE	100-01-6	138.14		1	800	2.27E-04									
226.	PARA-XYLYL CHLORIDE	104-82-5	140.61		60	10	1.11E+00									
569	PARAFORMALDEHYDE	30525-89-4	1000.00			100	1.00E-03									
523	PARALDEHYDE	123-63-7	132.30	0.99	25.3	120000	3.67E-05	0.00E+00	0.00E+00	125.0						
524	PARATHION	56-38-2	291.30	1.26	0.003		4.80E-05	0.00E+00	0.00E+00	375.0						
525	PCB-1254	11097-69-1	225.10	1.11	0.00008	0.08	2.96E-04	0.00E+00	0.00E+00	0.0						
527	PENTACHLOROBENZENE	608-93-5	250.34	1.61	0.0046		7.30E-03	6.30E-06	5.70E-02	277.0						
528	PENTACHLOROETHANE	76-01-7	202.30	1.67	4.4		2.10E-02	7.30E-06	6.60E-02	162.0	6.740	1378	197	2.2E-02		
529	PENTACHLOROPHENOL	87-86-5	266.40	1.98	0.00099		2.80E-06	6.10E-06	5.60E-02	310.0				3.9E-07		
965	PENTAERYTHRITOL	115-77-5	136.15		0.076	55000	2.48E-07									
526	PENTAERYTHRITOL TETRANITRATE	78-11-5	316.17			10	3.16E-05									
531	PHENACETIN	62-44-2	179.24	0.00	0.00072	760	2.23E-07	0.00E+00	5.70E-02	266.0				3.4E-03		
532	PHENANTHRENE	85-01-8	178.22	1.18	0.00021		6.05E-03	0.00E+00	0.00E+00	340.0						
533	PHENOL	108-95-2	94.10	1.07	0.341		4.54E-07	9.10E-06	8.20E-02	182.0	7.133	1516.79	174.95			0.81
815	PHENOL, 2,4-DINITRO-6-(1-METHYLPROPYL)-	88-85-7	240.24			20	1.20E-03									
534	PHENOTHIAZINE	92-84-2	199.28			1	1.99E-02									
536	PHENYL ISOCYANATE	103-71-9	119.13			1	1.19E-02									
780	PHENYL MERCURIC ACETATE	62-38-4	336.70				1.20E-08									
118	PHENYLACETIC ACID	103-82-2	136.14			16600	8.20E-07									
78	PHENYLACETIC PEROXIDE	78	152.00			1000	1.52E-05									
537	PHENYLENE DIAMINE(-m)	108-45-2	108.14	1.14	0.028		1.13E-08	0.00E+00	0.00E+00	284.0						
538	PHENYLENE DIAMINE(-o)	95-54-5	108.14	0.00	0.00797		1.13E-08	0.00E+00	0.00E+00	258.0						
539	PHENYLENE DIAMINE(-p)	106-50-3	108.14	0.00	0.0046		1.13E-08	0.00E+00	0.00E+00	267.0						
540	PHENYLHYDRAZINE	100-63-0	108.16			100	1.08E-04									
542	PHORATE	298-02-2	260.40		24.7		4.37E-07			110.5						
543	PHOSGENE	75-44-5	98.92	0.00	1394		1.71E-01	1.12E-06	1.08E-01	8.1	6.842	941.25	230			
H703	PHOSPHINE	7803-51-2	34		2000	100	8.95E-01									
885	PHOSPHORODITHIOIC ACID TRIETHYL ESTER	885	214.30			2	1.07E-04									
886	PHOSPHOROTHIOIC ACID TRIETHYL ESTER	3347-30-6	230.36			2	1.15E-04									
554	PHTHALIC ACID	88-99-3	166.14	1.59	120.8	2000	1.32E-02	6.80E-06	6.40E-02	72.6						
555	PHTHALIC ANHYDRIDE	85-44-9	148.11	0.00	0.0015		9.00E-07	8.60E-06	7.10E-02	284.0	8.022	2858.5	0			0.58
557	PHTHALIMIDE	85-41-6	147.10		117.5	2000	1.14E-02	0.00E+00	0.00E+00	69.5						
559	PICOLINE(2-)	109-06-8	93.12	0.96	10.4	10000	1.27E-04	9.60E-06	7.50E-02	128.8	7.032	1415.73	211.63			
560	PINENE(alpha-)	80-56-8	136.20	0.86	5	2	4.48E-01	0.00E+00	0.00E+00	155.0						
561	PIPERAZINE	110-85-0	86.14	0.00	3.72	10000	4.22E-05	0.00E+00	9.10E-02	146.0						
562	POLYBUTADIENE	562	1000.00			0.2	5.00E-03									
567	POLYETHYLBENZENE	567	1500.00			0.2	7.50E-03									
796	POLYETHYLENE	786	1500.00			0.2	7.50E-03									
858	POLYMERIC MATERIAL	858	5000.00			50000	1.00E-07									
870	POLYMERS CONTAINING NITROGEN	870	5000.00			0.2	2.50E-02									
568	POLYPROPYLENE	9003-07-0	20000.00			0.2	1.00E-01									
573	POLYSTYRENE	9003-53-6	20000.00			100	2.00E-04									
570	POLYURETHANE	570	20000.00			0.2	1.00E-01									
788	POLYVINYL ACETATE	9003-20-7	125000.00			0.2	6.25E-01									

KEY COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
789 POLYVINYL ALCOHOL	9002-89-5	120000.00			20000	6.00E-06									
785 POLYVINYL CHLORIDE	785	20000.00			0.2	1.00E-01									
574 POLYVINYLIDENE CHLORIDE	574	20000.00			0.2	1.00E-01									
575 PROPYNE	74-98-6	44.09		760	2000	2.20E-02									
575 PROPIONALDEHYDE	123-38-6	58.08	0.81	300	20000	1.15E-03	1.14E-05	1.02E-01	49.5						0.43
577 PROPIONIC ACID	79-09-4	74.09		10	20000	4.87E-05									
39 PROPIONITRILE	107-12-0	55.08		40	50000	2.75E-04									
578 PROPYL(-n) ACETATE	109-60-4	102.13	0.89	35	16000	2.94E-04	0.00E+00	0.00E+00	101.6	7.016	1282.28	208.60			0.13
579 PROPYL(-n) BENZENE	103-65-1	120.19	0.86	2.5	60	6.59E-03	0.00E+00	0.00E+00	159.0						
45 PROPYLENE	115-07-1	42.12		7600	200	2.11E+00									
581 PROPYLENE GLYCOL	57-55-6	76.11	1.04	0.3	20000	1.50E-06	1.02E-05	9.30E-02	188.0						
582 PROPYLENE OXIDE	75-56-9	58.08	0.00	524.5	30000	1.34E-03	0.00E+00	0.00E+00	34.3						0
583 PYRENE	129-00-0	202.30	1.27	4.20E-09	2	7.00E-09	0.00E+00	0.00E+00	404.0						
584 PYRIDINE	110-86-1	79.10	0.98	20	20000	2.36E-05	7.60E-06	9.10E-02	115.5	7.041	1373.80	214.98	4.1E-06		0.46
585 PYRIDINIUM BROMIDE	585	330.00			20000	1.65E-06									
597 RESERPINE	50-55-5	608.70	0.00	0.0052	2	2.00E-03	0.00E+00	3.20E-02	265.0						
598 RESORCINOL	108-46-3	110.11	0.00	0.00026	2000	1.88E-08	8.70E-06	7.80E-02	280.0						
552 S,S,S-TRIBUTYL PHOSPHOROTRITHIOATE	78-48-8	314.54			2	1.57E-04									
545 S-4-CHLOROCYCLOHEXYL-O,O-DIMETHYL PHOSPH	545	346.00			2	1.73E-04									
970 S-CYLCOHEXYL o,o-DIMETHYL PHOSPHORODITHI	970	240		0.00076	2	1.20E-04									
546 S-ETHYLSULFINYLMETHYL O,O-DIISOPROPYL PH	5827-02-4TH	304.45			2	1.52E-04									
969 S-ETHYLSULFINYLMETHYL o,o-DIISOPROPYL PH	969	320		0.00076	2	1.60E-04									
635 SIMAZINE	122-34-9	201.70		0.00000000	2	8.09E-10									
442 SODIUM DODECYLBENZENE SULFONATE	25155-30-0	284.10			20	1.42E-05									
795 SODIUM FORMATE	141-53-7	68.01			40000	1.70E-09									
869 SODIUM HYDROXIDE	869	40.00			1000000	4.00E-11									
890 SODIUM NITRATE	890	69.00			100000	6.90E-10									
883 SODIUM SULFATE	883	142.06			330000	4.30E-10									
822 STRYCHNIDIN-10-ONE,2,3-DIMETHOXY-	357-57-3	394.45			27000	1.46E-08									
604 STYRENE	100-42-5	104.20	0.90	7.3		3.30E-03	8.00E-06	7.10E-02	145.0	7.140	1574.51	224.09			0.06
41 SUCCINIC ACID	110-15-6	118.09			68000	1.74E-09									
427 SUCCINIMIDE	123-56-8	99.10			300000	3.30E-08									
134 SULFANILIC ACID	121-47-1	173.20			10800	1.60E-06									
64 SYM-DIETHYLDIPHENYL UREA	85-98-3	268.39			2	1.34E-02									
868 TARS	868	400.00			0.2	2.00E-03									
928 TETRACHLOROQUINONE	928	246		0.076	2	1.23E-02									
614 TETRACHLOROBENZENE(1,2,3,4)	634-66-2	215.90	0.00	0.019	2	2.70E-03	0.00E+00	0.00E+00	254.0						
615 TETRACHLOROBENZENE(1,2,3,5)	634-90-2	215.90	0.00	0.03	2	4.26E-03	0.00E+00	0.00E+00	246.0						
616 TETRACHLOROBENZENE(1,2,4,5)	95-94-3	215.90	1.86	0.03	2	4.26E-03	0.00E+00	0.00E+00	246.0						
617 TETRACHLOROETHANE(1,1,1,2)	630-20-6	168.00	1.60	6.5		2.00E-03	7.90E-06	7.10E-02	146.3	6.898	1365.88	209.74	4.6E-03		
618 TETRACHLOROETHANE(1,1,2,2)	79-34-5	168.00	1.60	6.5		3.80E-04	7.90E-06	7.10E-02	146.2	6.631	1228.1	179.9	5.8E-02		
619 TETRACHLOROETHENE	127-18-4	165.90	0.00	18.6		2.90E-02	8.20E-06	7.20E-02	121.0	6.976	1386.92	217.53	1.7E-06		0
620 TETRACHLOROPHENOL (2,3,4,6)	58-90-2	231.90	0.00	0.89		4.53E-06	0.00E+00	0.00E+00	164.0						
621 TETRACHLOROPHENOL (2,3,5,6)	935-95-5	231.90	0.00	.01	2	1.11E+02	0.00E+00	0.00E+00	26.1						
622 TETRACHLOROPROPENE (1,1,2,3)	10436-39-2	179.85			2	8.99E-03									
623 TETRAETHYL LEAD	78-00-2	323.45		0.35		8.09E-02									
H698 TETRAETHYLDITHIOPYROPHOSPHATE	3689-24-5	322.34		0.00000035	20	7.63E-09									
624 TETRAETHYLENE GLYCOL	112-60-7	194.26		1	20000	1.28E-05									
625 TETRAHYDROFURAN	109-99-9	72.12	0.88	72.1		4.90E-05	1.05E-05	9.80E-02	67.0	5.995	1202.29	226.25			
H704 THIOSEMICARBAZIDE	79-19-6	91.14		0.01	20000	6.00E-08									
627 THIOUREA	62-56-6	76.12	1.41	145		1.60E-04	0.00E+00	1.07E-01	182.0						
628 TOLUENE	109-88-3	92.00	0.87	30		6.68E-03	8.60E-06	8.70E-02	110.6	6.954	1344.8	213.48			0.12

KEY	COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS A	B	C	UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
629	TOLUENE DIAMINE(2,4)	95-80-7	122.00	1.11	0.001	2000	8.03E-08	0.00E+00	0.00E+00	0.0						
630	TOLUENE DIISOCYANATE(2,4)	584-84-9	174.16	1.20	0.08		8.30E-06	6.20E-06	6.10E-02	251.0						
123	TOLUENE-2,4-DIAZO-BIS-META-TOLUENEDIAMIN	123	428.00			1000	4.28E-05									
632	TOLUIC ACID (para-)	99-94-5	136.16		0.00031		5.60E-09	0.00E+00	0.00E+00	275.0						
633	TOLUIC ALDEHYDE	122-78-1	120.14	1.03	0.16	100	2.53E-04	0.00E+00	0.00E+00	204.0						
69	TOLUIDINE (-O)	95-53-4	107.70	0.00	0.242		2.30E-06	7.50E-06	7.30E-02	0.0						
634	TOXAPHENE	8001-35-2	414.00	1.11	0.3		4.89E-03	0.00E+00	0.00E+00	0.0						
544	TRIBROMOMETHYLPHOSPHATE	544	346.67			10	3.47E-05									
636	TRICHLORO-(1,1,2)-TRIFLUOROETHANE-(1,2,2	76-13-1	187.40	1.56	300		4.35E-01	8.20E-06	7.80E-02	48.0	6.880	1099.9	227.5			
637	TRICHLOROBENZENE(1,2,4)	120-82-1	181.50	0.00	0.18		1.42E-03	0.00E+00	0.00E+00	213.0						
638	TRICHLOROBENZENE(1,3,5)	108-70-3	181.50	0.00	0.23		2.09E-02	0.00E+00	0.00E+00	208.5						
640	TRICHLOROBUTANE(1,2,3)	18338-40-4	161.46	0.00	4.39	0.2	4.66E+00	7.20E-06	6.60E-02	0.0						
641	TRICHLOROETHANE(1,1,1)	71-55-6	133.40	1.35	123		3.00E-02	8.80E-06	7.80E-04	81.0	8.643	2136.6	302.8			
642	TRICHLOROETHANE(1,1,2)	79-00-5	133.40	0.00	25		7.42E-04	8.80E-06	7.80E-02	74.1	6.951	1314.41	209.20			
644	TRICHLOROETHYLENE	79-01-6	131.39	1.46	75		9.10E-03	9.10E-06	7.90E-02	87.0	6.518	1018.6	192.7	4.1E-06		
645	TRICHLOROFLUOROMETHANE	75-69-4	137.40	0.00	796		5.83E-02	9.70E-06	8.70E-02	23.8	6.884	1043.004	236.88			
646	TRICHLOROPHENOL(2,4,6)	88-06-2	197.46	0.00	0.0073		1.77E-05	0.00E+00	0.00E+00	244.5						
648	TRICHLOROPROPANE(1,1,1)	7789-89-1	147.43	0.00	3.1		2.90E-02	7.90E-06	7.10E-02	107.0						
649	TRICHLOROPROPANE(1,1,2)	598-77-6	147.43		6.64		2.90E-02			140.0						
650	TRICHLOROPROPANE(1,2,2)	3175-23-3	147.38		1.37		2.90E-02			124.0						
651	TRICHLOROPROPANE(1,2,3)	96-18-4	147.40	0.00	3		2.80E-02	7.90E-06	7.10E-02	156.0	6.903	788.2	243.23		550	
653	TRICHLOROPROPENE (1,1,2)	653	145.40			2	7.27E-03									
654	TRIETHYLAMINE	121-44-8	101.22		400	20000	2.66E-03									
655	TRIETHYLENE GLYCOL	112-27-6	150.20		1	20000	9.88E-06									
656	TRIFLUOROETHANE(1,1,1)	656	84.00		9241	2	8.40E+01			-47.3						
657	TRIMELLITIC ANHYDRIDE	552-30-7	192.13		0.0031		4.10E-06	0.00E+00	0.00E+00	242.5						
994	TRIMETHYLAMINE	75-50-3	59.11		1520	100000	1.18E-03									
658	TRIMETHYLBENZENE (1,3,5)	108-67-3	120.20		1.86	2	1.47E-01									
659	TRINITROTOLUENE(2,4,6)	118-96-7	227.10		0.046	1000	1.37E-05									
660	TRIPHENYL PHOSPHINE	603-35-0	262.30			2	1.31E-04									
267	TRIPHENYLPHOSPHINE NICKEL CARBONYL	267	377.00			10	3.77E-03									
661	UREA	57-13-6	60.06	1.34	6.69	2000	2.64E-04	1.37E-05	1.22E-01	133.0						0.11
662	URETHANE	51-79-6	89.09	0.00	10	20000	5.86E-05	1.06E-05	8.89E-01	-40.3	7.421	1758.21	205			
663	VALERIC ACID	109-52-4	102.13		1	2000	6.72E-05									
664	VINYL ACETATE	108-05-4	86.09	0.93	115		6.20E-04	9.20E-06	8.50E-02	73.0	7.210	1296.13	226.66			0.2
665	VINYL CHLORIDE	75-01-4	62.50	0.91	2660		8.60E-02	1.23E-05	1.06E-01	-12.0						
671	XYLENE	1330-20-7	106.20		8.5		5.25E-03									
668	XYLENE(-m)	108-38-3	106.16	0.86	8		5.20E-03	7.80E-06	7.00E-02	139.0	7.009	1426.266	215.11			0.008
669	XYLENE(-o)	95-47-6	106.17	0.88	591		5.27E-03	0.00E+00	0.00E+00	144.4	6.998	1474.679	213.69			0.008
670	XYLENE(-p)	106-67-9	106.16	0.86	9.5		5.27E-03	0.00E+00	0.00E+00	138.4	6.990	1453.430	215.31			0.11
488	alpha-CHLORO-beta-METHYLNAPHTHALENE	86-52-2	176.65			2	8.83E-03									
76	alpha-METHYLSTYRENE (-4)	98-93-9	118.19			2	5.91E-03									
477	alpha-PICOLINE	1333-41-1	93.14			20000	4.65E-07									
507	beta-PROPIOLACTONE	57-57-8	72.10		3.4	350000	9.22E-07									
226	m-XYLYL CHLORIDE	620-19-9	140.60			10	1.41E-03									
945	n-HEPTACOSANE	593-49-7	380.75		0.00076	2	1.90E-04									
389	n-HEXADECANE	544-76-3	226.39			0.0009	2.52E+01									
995	n-HYDROXYMETHYL-n-CHLOROMETHYLETHYL-AMIN	995	109.5		0.076	50	2.19E-04									
468	n-TRICOSANE	629-50-5	184.31			2	9.22E-05									
300	p,p'-DICHLOROBENZOPHENONE	90-98-2	251.11		0.00000287	0.2	4.74E-06			353.0						
125	p-AMINO-p'-METHYLAZOBENZENE	125	212.00			2	1.06E-02									
479	p-CHLORO-N-METHYLBENZAMIDE	479	169.61			2000	8.48E-06									

KEY	COMPOUND NAME	CAS #	M.W.	DENSITY (g/cc)	VAP.PRESS (mmHg)	SOLUBILITY (mg/l)	H LAW CONST. (atm-m3/mol)	DIFF.WATER (cm2/sec)	DIFF.AIR (cm2/sec)	BOILING POINT (deg.C)	VAPOR PRESSURE COEFFICIENTS			UNIT RISK VALUE	ADI in AIR (g/m3)	BOD/COD RATIO
											A	B	C			
161	p-CHLORO-p'-METHYLBIPHENYL	1667-11-4	202.69			2	1.01E-02									
353	p-CHLOROBENZOPHENONE	134-85-0	216.67		2.60E-06		3.46E-09			330.0						
208	p-CHLOROBENZOTRICHLORIDE	5216-25-1	229.87			0.2	1.15E-01									
355	p-CHLORODIPHENYL THIOETHER	7005-72-3	204.57			2	1.02E-02									
58	p-CHLOROMETHYL BENZOATE	1126-46-1	170.60			0.2	8.53E-02									
53	p-CHLOROMETHYL PHENYLHYDRAZINE	62	157.00			50	3.14E-04									
115	p-CYANOBENZYL ALCOHOL	116	119.00			5000	2.38E-06									
736	p-DIETHYLBENZENE	25340-17-4	134.22			2	6.71E-03									
79	p-METHOXYPHENOL	150-76-5	124.15			40000	3.10E-07									
266	p-METHYL-p'-METHYL TRIPHENYL PHOSPHINE	266	292.30			2	1.46E-02									
144	p-NITROBENZENESULFONYL CHLORIDE	98-74-8	221.58			50	4.43E-04									
102	p-NITROBENZYL ALCOHOL	619-73-8	153.08		10	10000	2.01E-04									
163	p-PHENYLPHENOL	92-69-3	170.20		10	700	3.20E-03									
104	p-THIOBENZYL ALCOHOL	100-53-8	124.21			1000	1.24E-05									
135	p-TOLUIDINE	106-49-0	107.17		1	7400	1.91E-05									